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Interim Report

EFFECT OF FUEL ADDITIVES ON THE CHEMICAL AND PHYSICAL CHARACTERISTICS OF PARTICULATE EMISSIONS IN AUTOMOTIVE EXHAUST

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Prepared for:

Division of Chemistry and Physics
National Air Pollution Control Administration
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Project Officer

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16. Abstracts
Methods were developed of generating, collecting, and analyzing particulates in automotive engine exhaust by a means sufficiently accurate and reproducible to allow determination of the effects of fuel additives on exhaust particulate size, concentration, and composition. The clean (new) engine must be conditioned with the test fuel for a period of at least 75 hours under cycled conditions before stable gaseous and particulate emissions are achieved. An air dilution chamber was designed which allows for cooling, dilution, and mixing so that representative particulate samples can be obtained at a sampling station which is essentially equivalent to 8-10 feet downstream of the end of the exhaust pipe on a vehicle at highway speeds. Temperature of the diluted exhaust at the sampling station was around 110 F. A 1970 Chevrolet 350 CID engine of 9.0:1 compression ratio with a standard exhaust system attached, was loaded by means of an engine dynamometer. Sampling was conducted with the engine operating at 2250 RPM and 17.0" Hg manifold vacuum from 4 of the 8cylinders. A few sampling runs were conducted under mild cycled conditions consisting of several cruise modes. Special analysis techniques were developed for the analysis and characterization of exhaust particulates. The data suggest a very significant effect of fuel additives, primarily TEL, on exhaust particulate size, concentration and composition. Significant differences are observed with minor changes in other fuel additives.

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The Dow Chemical Company
Midland, Michigan

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July 1969 to June 1970

for

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National Air Pollution Control Administration
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FOREWORD

This report was prepared by the Transportation Research Group, Organic Chemicals Department, The Dow Chemical Company, Midland, Michigan under Contract CPA-22-69-145. This work was administered under the direction of the National Air Pollution Control Administration, Environmental Health Service, with Dr. Jack Wagman as project officer.

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ABSTRACT

This report describes work carried out on a research program to develop methods of generating, collecting, and analyzing particulates in automotive engine exhaust by a means sufficiently accurate and reproducible to allow determination of the effects of fuel additives on exhaust particulate size, concentration, and composition. It has been determined that it is essential to condition the clean (new) engine with the test fuel for a period of at least 75 hours under cycled conditions before stable gaseous and particulate emissions are achieved. An air dilution chamber has been designed which allows for cooling, dilution, and mixing so that representative particulate samples can be obtained at a sampling station which is essentially equivalent to 8-10 feet downstream of the end of the exhaust pipe on a vehicle at highway speeds. Temperature of the diluted exhaust at the sampling station is around 110°F.

The work reported has been conducted using a 1970 Chevrolet 350 CID engine of 9.0:1 compression ratio with a standard exhaust system attached, loaded by means of an engine dynamometer. Sampling has been conducted with the engine operating at 2250 RPM and 17.0" Hg manifold vacuum from 4 of the 8 cylinders. A few sampling runs have been conducted under mild cycled conditions consisting of several cruise modes.

Special analysis techniques have been developed for the analysis and characterization of exhaust particulates. The details of these techniques are included in this report.

The data gathered while substantiating the applicability of the techniques developed, in addition suggest a very significant effect of fuel additives, primarily TEL, on exhaust particulate size, concentration and composition. Significant differences are observed with minor changes in other fuel additives. These observations emphasize the need for a study of particulate emissions from vehicles operated under simulated driving conditions.

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I. INTRODUCTION

This is an interim report covering our first year's efforts to develop a fundamental understanding of the nature of particulate emissions from automotive internal combustion engines. In general terms, we have investigated the effect of well-defined fuel additives on the characteristics of particulate and gaseous emissions from a dynamometer-loaded automotive engine. The study has involved proper engine conditioning to provide stable and repeatable gaseous and particulate emissions, the design and installation of a suitable particulate collection system, and the examination of the effect of steady-state operation versus mild cyclic operation of the engine on exhaust emissions, both gaseous and particulate.

A well-defined research fuel, namely Indolene HO, has been used as the base fuel throughout these studies. An anti-knock compound (Tetra Ethyl Lead), lead scavengers, and a detergent additive, have been investigated to date.

Collection, classification, and analysis of the exhaust particulates have been the most challenging tasks in this study. An exhaust-air dilution chamber has been used which forms the basis for the particulates data reported herein. We attempted to sample the raw exhaust to obtain particulate samples. This effort failed. It became apparent that air dilution of the exhaust was essential in order to obtain particulate samples which were somewhat representative of those encountered from actual vehicles. A dilution tube was designed and installed which provides approximately 12:1 dilution ratio of air to exhaust gas. The tube is of sufficient length that nearly all particles 20 μ and larger separated before entering the sampling zone. The tube was constructed in several pieces so that it could be easily disassembled, cleaned, and reassembled, thus allowing collection of all particles emanating from the exhaust pipe. Initially, the complete exhaust from the engine was diverted through the dilution tube. However, it became apparent that adequate dilution ratios to avoid condensation in the Andersen samplers, to reduce particle agglomeration, and obtain reasonable sampling temperature, and yet obtain proper filtration of the diluent air could not be achieved with such high exhaust volumes. Consequently, it was decided to use only the four left bank cylinders of the V-8 engine for exhaust sampling. Reduced loading of the engine was deemed inappropriate as idle to 30 MPH cruise conditions would not be relevant. In addition, we recognized the need for cycled operation sampling in the near future.

It is apparent that the definition of an exhaust particle is somewhat dictated by the collection system employed, i.e., particulates are defined as those solid and liquid materials collected in the specific device and under the specific conditions of the sampling hardware. Several particulate sample collection methods could have been employed. We decided to use the Andersen Impact Sampler Model 0203 because it provided reasonably large samples, size classification and is relatively insensitive to operator variables. The Andersen provides only a proportional sample of the air-exhaust mixture. However, stable sampling zone conditions have been achieved with the dilution system.

This report covers, in detail, the procedures employed in generating, collecting and analyzing exhaust particulates. It is apparent that fuel consumption, engine condition, engine loading, and collection procedures greatly affect particulate emissions results. As with hydrocarbon emissions, it will be essential to define specific procedures in order to obtain meaningful and reproducible particulate emissions data.

The relevance of this study to actual vehicles and the effect mileage accumulation procedures and sampling cycle will have on particulate emissions therefrom has not yet been established. This work does, we feel, provide a sound basis from which meaningful studies in that direction can be based as sound, reproducible, collection and analytical techniques have been developed.

II. CONCLUSIONS

This interim report covers only the first phase of work in a continuing program to develop a fundamental understanding of particulate emissions from the automotive engine. In order to develop sampling and analytical proficiency, it was found necessary to limit the work to one make of V-8 engine, a well-defined operating condition of that engine, and a well-defined particulate sampling system. The evaluations were conducted on an engine attached to a dynamometer programmed to simulate typical engine cruise conditions (60 MPH, road load). None of the work in this phase involved complete vehicle system operation. It was recognized that particulate emissions could be sensitive to engine condition, operating mode, etc., as are gaseous emissions. The particulate sampling device also somewhat defined the particles collected for study.

Conclusions within the defined scope of study are:

1. A collection and classification system was developed which, when combined with the analytical capabilities developed under this study, resulted in the ability to ascertain significant differences in exhaust particles with minor changes in fuel additives. Thus, the basic objective of this initial study was achieved.

2. In the series of 16 tests reported the following fuel additive effects were noted.

    A. Increased concentration of Tetra Ethyl Lead from trace levels to 3.0 ml/gal resulted in increased particle emissions, increased combustion chamber deposits, and hydrocarbon emissions.

    B. Increased concentration of TEL from trace levels to 1.5 ml/gal showed a disproportionate increase in hydrocarbon emissions and combustion chamber deposits, but an unexpectedly small increase in particulate emissions.

C. Lead scavengers had a pronounced effect on exhaust particulates and emissions, and on combustion chamber deposits. The more effectively the scavenger did its job (lower combustion chamber deposits), the lower were the hydrocarbon emission levels and the greater the particulate emission levels (motor mix, EDB, and EDC have been evaluated).

D. The use of a detergent additive to the 3.0 ml/gal TEL motor mix base fuel, decreased deposits and hydrocarbon emission levels, but increased particulate emissions when compared to the base fuel.

E. Some experiments using cycled operation showed only a slight effect on particulate emission levels compared to steady-state operation probably due to the fact that our cycled sequence was a combination of several cruise conditions.

F. The percentage of organics associated with exhaust particulates increased with decreasing particle size.

G. The percentage of organic material associated with exhaust particles increased with decreasing TEL concentration. However, see page 68.

H. The exhaust particle size distribution was affected by TEL, scavengers, additives, and cycling.

I. In general, 50% of the mass of exhaust particles were smaller than 0.1 micron (MMED).

III. TEST EQUIPMENT AND PROCEDURES

The test equipment arrangement used for this study is as shown schematically in Figure 1. The engine, dynamometer, exhaust system, and dilution tube inlet are located in the dynamometer cell. The cell air is filtered, and heated when necessary. Sufficient air capacity is available to keep a positive pressure in the room and to replace the cell air every 30 seconds. The remainder of the dilution tube is located adjacent to the engine cell in an air-conditioned room which also houses all instrumentation with the exception of the NO/NO_2 analyzer which is in the test cell.

The engine used for all experimental runs made during the period of the report was a 1970 Chevrolet 350 CID engine with the following specifications:

Displacement	350 cubic inches
Horsepower	255 @ 4800 rpm
Carburetor	2 barrel Rochester
Compression Ratio	9.0:1
Bore	4.0"
Stroke	3.48"
Spark Plugs	AC R45S
Plug Gap	.035"
Point Dwell	28-32°
Timing	4° BTC

The right bank of cylinders is attached to an exhaust pipe which is exhausted from the room through the cell exhaust system. The left bank of cylinders is connected to a typical exhaust system which is run into the dilution tube. The

Flow Diagram for Engine Exhaust Particulate Collection

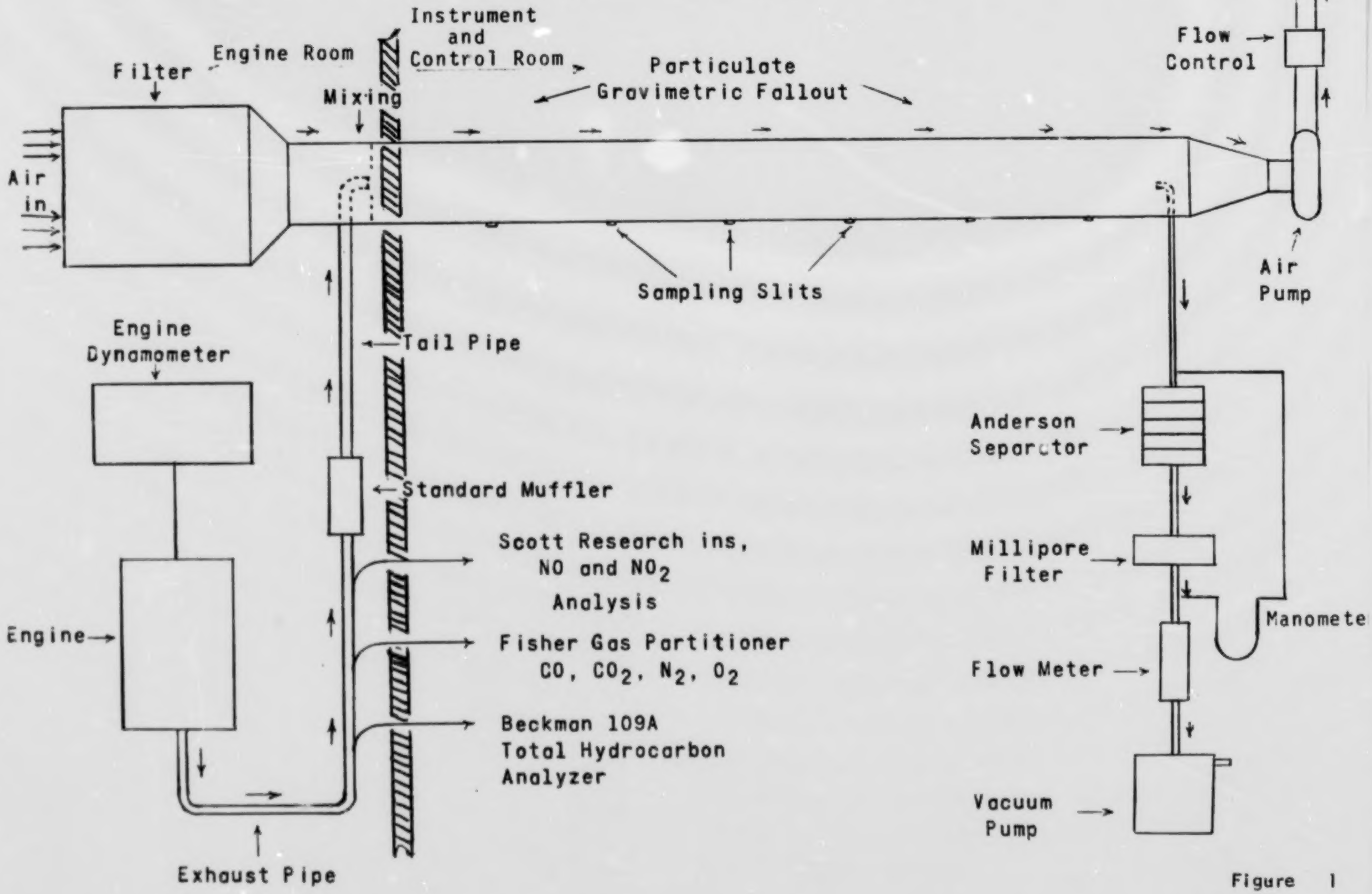

Air out
Flow Control
Instrument and Control Room
Engine Room
Filter
Particulate Gravimetric Fallout
Mixing
Air in
Air Pump
Sampling Slits
Engine Dynamometer
Tail Pipe
Standard Muffler
Scott Research ins, NO and NO$_2$ Analysis
Fisher Gas Partitioner CO, CO$_2$, N$_2$, O$_2$
Beckman 109A Total Hydrocarbon Analyzer
Engine
Exhaust Pipe
Anderson Separator
Millipore Filter
Manomete
Flow Meter
Vacuum Pump

Figure 1

cross-over heating passages under the carburetor are plugged. Specific components of the exhaust assembly used for each run are:

Exhaust Manifold	1-5/8" ID 20" long
Exhaust Pipe	Walker 97836 2-1/2" ID 67" long
Muffler	Walker 21530 W5798 21" long
Tail Pipe	1-5/8" ID 76" long

A Meriam Laminar Flow Element Model 50MC-2-45F air flow measurement unit is attached to the carburetor via a flexible rubber hose for air consumption measurements. An A/C paper filter element is used on the Meriam to filter incoming air.

The engine-dynamometer set-up is completely instrumented to monitor and/or control coolant temperature, oil temperature, manifold vacuum, fuel flow rate, air flow rate, RPM, load, etc.

Amoco 100, SAE 30 lubricating oil has been used in all experimental runs. This oil was chosen as a minimum acceptable oil with a low additive package content so that contributions of the oil to the particulate material would be minimized. This oil has the following trace metal analysis:

Table 1

ENGINE OIL, TRACE METAL ANALYSIS

	Wt. %		Wt. %
Fe	.0002	Mn	.0001
Ni	<.0001	Pb	.0006
Cu	<.00002	Cr	<.0001
Al	.0001	Sn	<.0001
Ca	.0017	Zn	.081
Si	.0001	Ti	<.0001
Mg	.089	P	.05
		Mo	<.0001

and the following physical properties:

Table 2

ENGINE OIL, PHYSICAL PROPERTIES

Gravity, °API	26.4
Flash, °F	450
Pour, °F	0
Viscosity 100°F	555 SUS
210°F	66 SUS
V.I.	95
Color, ASTM	5
Sulfated Ash, % Wt.	1.0
Carbon Residue, % Wt.	1.3

Before each run is begun, the engine is thoroughly cleaned and inspected. The heads are removed and deposits from the heads and piston tops from the previous run are removed for weighing and analysis. The heads are then cleaned with solvent. Valves are removed and inspected. Generally three runs can be made between each valve refacing and re-seating, in which case the valves are cleaned of deposits and only a light valve lapping is necessary in order to obtain good seating and seat width. Each valve guide clearance is checked for tolerances and the valve end is observed for wear.

New seals are installed on each valve stem. The heads are reassembled and torqued to the manufacturers specifications. A new exhaust system, oil filter, oil, points, plugs, and condenser are installed. The dwell and timing are checked and set to manufacturers specifications. The fuel lines are purged with clean dry air before the new test fuel is pumped to the engine. The carburetor is then adjusted for best idle vacuum.

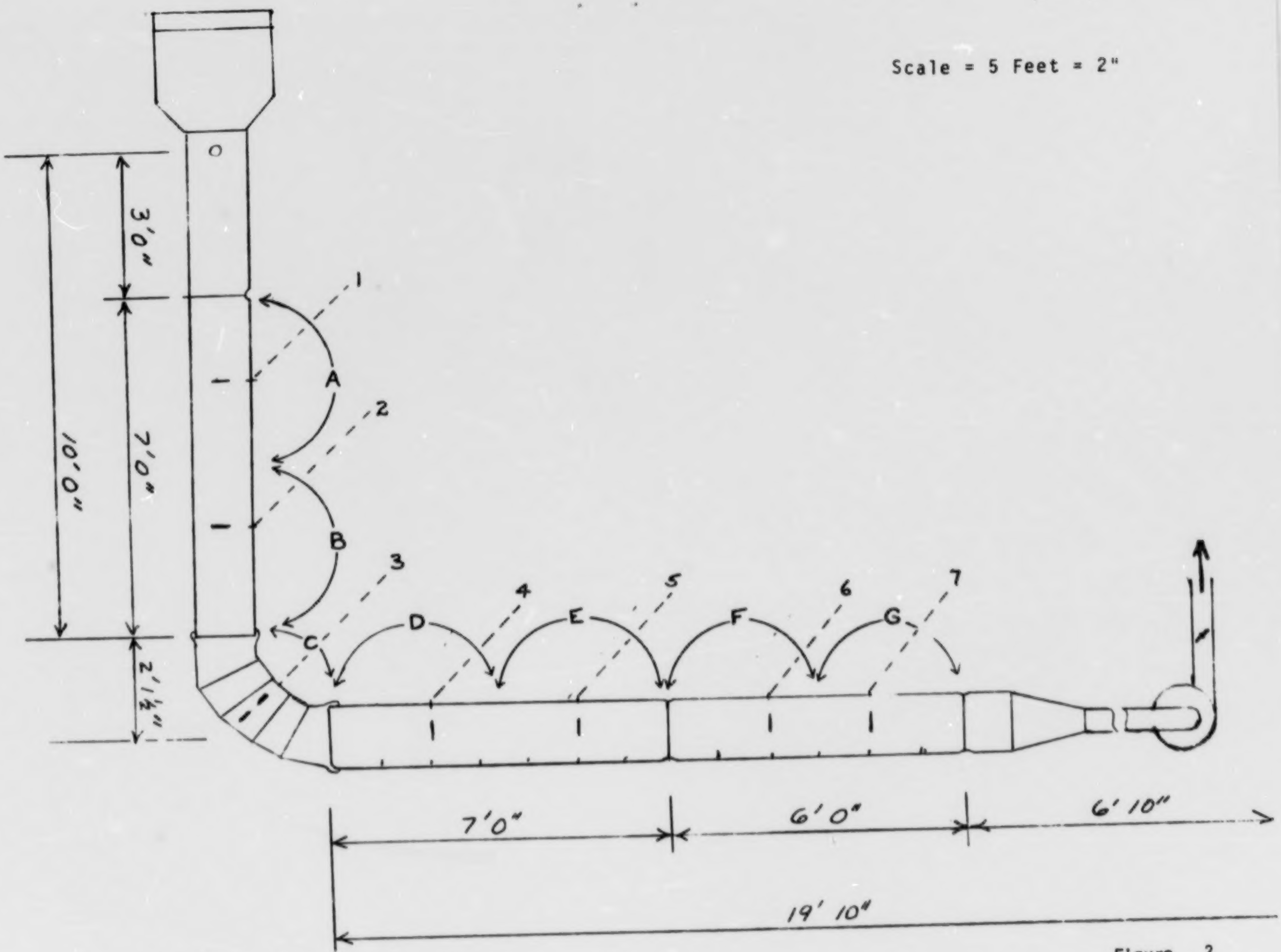
The dilution tube is an extruded pipe made of polyvinyl chloride. It is 16" in diameter with a 1/4" wall thickness. In total it is 27 feet long which includes a 90° bend section as shown in Figure 2. A 7 foot air induction head which houses the air filter assembly, exhaust inlet elbow, and mixing baffle is mounted in the wall between the instrument room and the engine test cell. The mixing baffle consists of a flat sheet metal donut attached perpendicular to the tube axis to the inside wall of the induction head which acts to force the incoming diluent air through the 8" hole in the center of the baffle, thus mixing with the exhaust gas. The exhaust elbow enters at 90° to the tube axis and is bent 90° so that the flow axis of the exhaust gas parallels the axis of the dilution tube. The exit end of the exhaust elbow is in the same plane as the baffle.

An exhaust fan is located at the exit end of the dilution tube. A throttle plate is located in the dilution tube exit assembly following the fan in order to allow control of flow volumes through the tube. The dilution tube consists of several sections with butt joints which are taped during assembly. This construction allows for easy removal, cleaning, and inspection of the complete dilution tube after each run. Samples swept from each tube section are designated as shown in Figure 2.

Several small slits have been cut in the bottom of the tube along its length. Special glass collecting plates were fabricated which are attached to the outside of the tube under each slit to collect particulate samples. Such samples are referred to herein as "slit samples." Slit locations and numbers are shown as short dashed lines perpendicular to the tube axis in Figure 2.

Initially, a simple 24" x 24" flat fiberglass air filter was used to filter the diluent air coming into the tube. Particulate loading in the tube and sampling systems observed with diluent air only was nearly as high as that obtained during a run

Scale = 5 Feet = 2"


3'0"
7'0"
10'0"
2'1½"
1
2
3
4
5
6
7
A
B
C
D
E
F
G
7'0"
6'0"
6'10"
19'10"

PARTICULATE SAMPLING TUBE

Figure 2

with a test fuel. This caused us to look for a better filter medium. As a result, we installed a Dri-Pak Series 1100 Class II PIN 114-110-020 untreated cotton filter assembly. This filter assembly is 24" x 24" and has 36 filter socks which extend to 36" in length. This filter will pass particles 0.3 μ in size and smaller. Pressure drop at 600 cfm flow rate is minimal.

The particulate proportional sampling zone is located at the exhaust end of the dilution tube. The sample probe elbows are located in the exhaust-air stream. Each probe is connected to an Andersen Impact Sampler Model 0203, a filter assembly, and a vacuum pump, in that sequence. The probes are 0.754" ID aluminum tubes. These sample tubes are located as shown in Figure 1. A Hg manometer is connected between the dilution tube probe and the exhaust side of the filter assembly and is used to monitor the pressure drop across the Andersen Samplers during the course of each run. A flow meter follows the filter and is used to monitor and regulate flow through the Andersens and filter during the run.

Each run consists of positioning the cleaned and washed tube, connecting slit collection plates, and connecting the cleaned Andersen Samplers and filter sampling equipment at the sampling zone. The engine is started and run on the new test fuel at idle for several minutes while temperatures, oil pressure, etc., are observed. The engine is then switched over to a cycling conditioning sequence. Unburned hydrocarbon levels are closely monitored during the first two hours of cycling which allows excellent scrutiny of engine condition.

The engine is run on the conditioning cycle for 75 hours to stabilize engine deposits, emission levels, and engine condition. The cycle is as follows:

Table 3

TEST ENGINE CONDITIONING SEQUENCE

Cycle	RPM	Time (Min.)	Vacuum ("Hg)	Decay
1	800	2.0	18.8	---
2	1070	13.0	16.4	1/2 min.
3	1615	20.0	17.2	1/2 min.
4	2125	13.0	14.3	1/2 min.
5	1070	12.0	16.4	1/2 min.

The sequence repeats after cycle 5. Unburned hydrocarbons, oxides of nitrogen, and all engine operating conditions are observed and recorded during the conditioning sequence of 75 hours.

After the 75 hour conditioning sequence, the exhaust pipe is connected to the inlet pipe to the dilution chamber while the engine is running. The particulate sampling run is then begun with the exhaust gas being put into the dilution chamber and mixed with diluent air from the dynamometer cell. Sampling is conducted for 48 hours with the engine running at 2250 RPM at 17.0" Hg intake vacuum. During this time unburned hydrocarbons and oxides of nitrogen are monitored and recorded as are the engine conditions and dilution tube conditions.

In several instances, the engine was run under cycling mode into the dilution chamber to determine the effect of cycling on the particulate emissions. In that case, the engine is shut down after the 48 hours steady-state run, the dilution tube is cleaned and reassembled as are the particulate samplers. The engine is then run under the same cycling mode as the conditioning sequence. The exhaust is again put into the dilution tube and samples collected as before, for 48 hours. The dilution air flow rate is not, however, changed to hold the 12:1 dilution factor used during steady-state sampling.

IV. EXHAUST GAS ANALYSIS AND SAMPLE COLLECTION

A. EXHAUST GAS

1. General

The engine exhaust gas is analyzed for oxygen, nitrogen, carbon monoxide, carbon dioxide, total and individual volatile hydrocarbons. The analysis is done by gas chromatography, chemical absorption, and a total hydrocarbon analyzer. Data reduction is by an IBM 1800 computer through a Bell Telephone ASR 33 Teletype interface.

a. Analytical Equipment

A Fisher Gas Partitioner is used for the analysis of oxygen, nitrogen, carbon monoxide, and carbon dioxide. The column system consists of a 6' hexamethyl phosphoramide and a 6-1/2' 13x molecular sieve in series.

Total hydrocarbons are obtained from a Beckman Model 109A Total Hydrocarbon Analyzer. The concentration of unsaturated hydrocarbons is determined by passing the sample through an absorption tube 1/2" x 8" filled with 30-60 mesh pink Chromosorb® impregnated with 50% mercuric perchlorate.

A Hewlett-Packard Model 5750 Gas Chromatograph with a hydrogen-flame detector is used for the analysis of individual volatile hydrocarbons. The column is a 20' x 3/16" O.D. filled with 20% Apiezon® L on 60-80 mesh pink Chromosorb and is programmed from 50°C to 250°C.

The output of each gas chromatograph is coupled with a Hewlett-Packard Model 3370A Digital Integrator which has an Ascii coded output to drive an ASR 33 Teletype and punch paper tape.

b. Sampling
A Neptune Dyna-Pump® is used to pull the sample from the exhaust pipe sampling point through 1/4" O.D. stainless steel tubing and transfers it to the total hydrocarbon analyzer and the gas sampling valves of the two gas chromatographs through 1/8" O.D. stainless steel tubing. A manifold system is provided to allow the operator to calibrate the equipment with the appropriate standards. (See Figure 1 for sample source information.)

c. Standardization
A gas mixture containing known concentrations of oxygen, nitrogen, argon, carbon monoxide, carbon dioxide, and n-hexane is used as a reference standard for the total hydrocarbon analyzer and the Fisher Gas Partitioner. A liquid sample containing a composite of ten representative hydrocarbons is injected into a 10 liter saran bag for the individual hydrocarbon analysis.

Component identification is done by peak retention time. Shifts in retention time and changes in detector response are compensated for by standardization preceding each series of samples.

d. Operation
The operator types the proper computer code and program number on the teletypewriter, injects the reference standard, and presses the integrator start button. As the peaks

emerge, the time and area information is encoded and stored on punched paper tape. Each succeeding exhaust gas is identified along with the total hydrocarbon level, and run in the same manner as the standard. When the series is finished, the punched tape is sent to the computer by teletype over regular telephone lines.

e. Data Reduction

A typical output format for the gas analysis is shown in Figure 3. Identification of the components in the standard is based upon each peak size in descending order. Estimated retention time is the up-dated time of each peak in the standard. Retention time windows are 4 seconds plus 2% of the retention time. Actual percent is a direct ratio of the area counts in the unknown sample to the area counts in the standard times the volume percent in the standard. The total percent actual will normally be 97-98% since water is removed form the saturated sample after the sampling valve.

A correction for the unresolved argon in oxygen is made based upon response factors and the amount of argon found in a number of exhaust gas samples by mass spectroscopy.

The actual percent is normalized to 100% in the next column or a moisture free basis, and an Exhaust Gas Analysis report is issued below. The air to fuel ratio is calculated from this analysis, the total hydrocarbon content, and the percent carbon in the fuel.

```
G. C. ANALYSIS - TECHNICAL DATA -                    6-29-70
GOV RUN #18 JUNE 27 1970
CYCLE #4 78.1 HRS
 HC 620. PPM

 PEAK     TIME          PCT. VOL.          COMPOUND
  NO.  ACT.   EST.   ACTUAL   NORM.    IDENTIFICATION


   1    54.    54.    0.000    0.000   COMPOSITE
   2    75.    75.   12.561   12.825   CARBON DIOXIDE
   3    92.   ---.    0.000    0.000   ----
   4   132.   132.    0.616    0.628   OXYGEN
                      0.900    0.919   ARGON
   5   147.   146.   82.001   83.724   NITROGEN
   6   202.   202.    1.863    1.902   CARBON MONOXIDE
                    -------  -------
                     97.941  100.000   TOTALS
                      2.059            BALANCE BY DIFFERENCE
                      2.059            TOTAL CONTAMINATION LEVEL

-----------------------------------------------------------------
-----------------------------------------------------------------

         EXHAUST GAS ANALYSIS             6-29-70

GOV RUN #18 JUNE 27 1970
CYCLE #4 76.1 HRS
 HC 620. PPM

 TIME  PERCENT  IDENTIFICATION

 132.      0.9  ARGON
 146.     83.7  NITROGEN
 132.      0.6  OXYGEN
 202.     1.90  CARBON MONOXIDE
  75.     12.8  CARBON DIOXIDE
         -----
         100.0  TOTAL

FRACTION CARBON IN FUEL 0.3625

TOTAL HYDROCARBON CONTENT  620. PPM.

AIR/FUEL RATIO 14.1
```

Figure 3

2. Oxides of Nitrogen

a. Equipment

Beckman Ultraviolet Analyzer
Beckman Infrared Analyzer
Recorder - Texas Instrument Company

The above pieces of equipment are in a single, self-contained unit built by Scotts Research Labs Inc., San Bernardino, California.

b. Calibrating Gases

Nitric oxide (3545 ppm in nitrogen)
Nitrogen dioxide (862 ppm in nitrogen)

These standard gases are furnished by Scotts Research Labs, Inc.

Nitrogen is used as zero calibrating gas.

c. Procedure

Before making NO, NO_2 measurements, the paper filters (Whatman #3) to each analyzer are changed and the Dri-Rite dryer in the exhaust sample is replaced.

Both analyzers are standardized using the appropriate calibrating gas at a constant flow. The zero standardizing is done using nitrogen as the calibrating gas using the same flow rate.

After the instrument is standardized, the exhaust gas is passed through the analyzer using the same flow rate as in the standardization step. The NO, NO_2 values are recorded by the dual pen Servo-riter recorder. Figure 1 indicates the source of the exhaust gas sample.

B. PARTICLES

Particulates are sampled in such a manner that all particulates emitted from the tail pipe are represented. The mass distribution is determined by weighing collected particulates after 48 hours sampling at the following locations:

1. Dilution tube slit collection plates
2. Dilution tube - each section
3. Andersen Samplers - 6 collection plates each
4. Filter (following Andersen Sampler)

Tube slit plates are simply weighed in and out, the difference being the mass of particles collected during the run. The dilution tube is disassembled and each section is carefully swept out with a camel hair brush onto a sheet of clean paper. The sample is then transferred to a tared sample bottle, which is weighed again to determine sample weight by difference.

The Andersen Sampler collection plates are weighed before and after the run, the difference being, again, sample weight.

Prior to use, the Millipore and fiberglass filters are stored in the instrument room which is temperature and humidity controlled. The filters are placed on the tray in a Mettler Analytical balance and are allowed to reach equilibrium, then weighed out to the fourth place.

After the test, the filters are removed from the holders and again allowed to reach equilibrium, noted by no further change in weight, then weighed to fourth place. This is done in the same room in which the papers are stored. The Millipore filters used are 142 mm type AAWP 0.8 μ. The fiberglass filters used are Gelman 0.3 μ Type A 2" diameter. The Millipore filters are used for most of the sample work, the fiberglass for special analytical processing.

The particulate samples follow a rather involved route for complete analysis. This is due to the fairly small quantity of particulate sample, notably in the smaller size ranges (below 15 μ) associated with the Andersen Sampler - filter portion of the sampling system as each sampler only gets ∿1/500th of the diluted stream. Three Andersens are used at a sampling rate of 1 cfm. An additional unit operates at 1/2 cfm and is provided to the Microscopy Lab for analysis. This is used to facilitate Stereoscan/X-ray analysis of larger crystals which are less impact damaged in the Andersen.

C. COMBUSTION CHAMBER DEPOSITS

The deposits in the combustion chamber and on the top of the pistons are collected after each test tun. Head bolt and water passage holes are taped to avoid contamination and sample loss. The deposits are scraped off using a putty knife and round nosed spatula into a large sheet of heavy paper. The valves are left in the head during deposit removal. The deposits are similarly removed from the piston tops. The deposits collected are transferred to tared sample bottles, which are weighed and the run number, date, and sample weight recorded on the bottle and in the sample log book.

V. RESULTS

A. INTRODUCTION

Much of the data to be presented in this section of the report bears on several topics. Mass spectrometry, for example, provides an analysis of the effect of particle size on the amount of NH_3, H_2O, HCl, and total organics present. Ultraviolet Analysis provides information on the relative amounts of aromatic organics including PNA's. In order to provide a basic picture of the results from each of these various techniques, they will be reported and discussed separately. Comparisons will be drawn in the Discussion Section which follows.

For convenience, all data are presented by referring to run numbers rather than the specific test fuel used for each such run. The test fuels are shown in table 4 on the attached fold-out reference sheet.

B. Dilution Tube

1. Temperature Profile

The temperature of the exhaust gas-diluent air stream 1" into the dilution tube at four points along the tube are shown for all runs below in Table 5. Thermocouple location is shown in Figure 4. Temperature in °F.

Table 5

Run #	TC #9	TC #10	TC #11	TC #12	Diluent* Air
3	110	106	108	107	82
4	106	103	104	103	78
5	106	103	103	103	79
6	114	104	110	110	96
7	125	118	120	120	95
8	120	115	115	115	80
9	127	115	120	115	80
11	117	113	113	108	88
13	125	120	120	120	95
16	126	115	118	118	82

TC - Thermocouple
* - Test Cell Air Temperature

B. DILUTION TUBE

1. Temperature Profile

The temperature of the exhaust gas-diluent air stream 1" into the dilution tube at four points along the tube is shown for all runs below in Table 5. Thermocouple location is shown in Figure 4. Temperature is in °F.

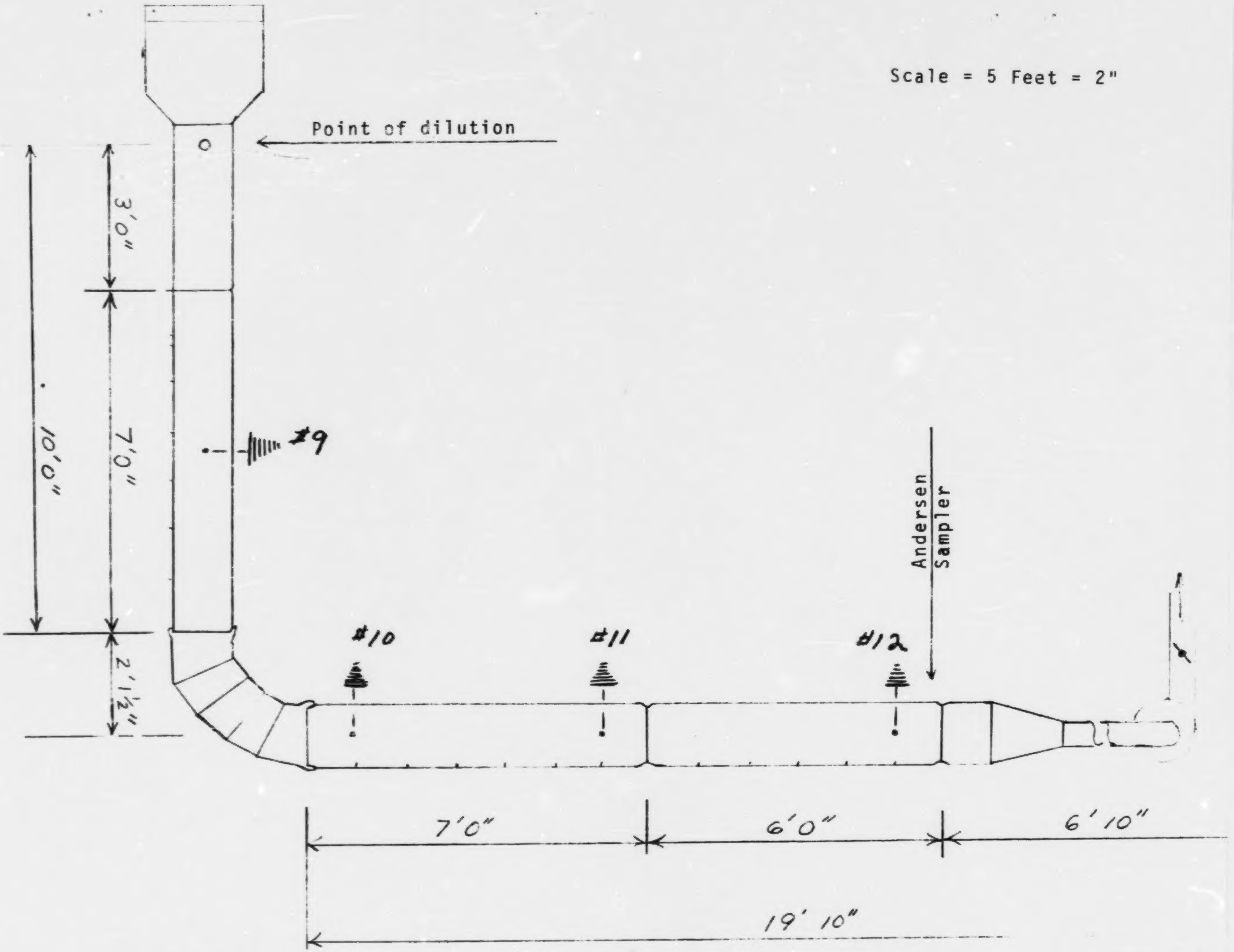
Table 5

DILUTION TUBE TEMPERATURE PROFILE DURING STEADY-STATE OPERATION SAMPLING

Run #	TC #9	TC#10	TC #11	TC #12	Diluent* Air
3	110	106	108	107	82
4	106	103	104	103	78
5	106	103	103	103	79
6	114	104	110	110	96
7	125	118	120	120	95
8	120	115	115	115	80
9	127	115	120	115	80
11	117	113	113	108	88
13	125	120	120	120	95
16	126	115	118	118	82

TC - Thermocouple

* - Test cell air temperature


Scale = 5 Feet = 2"
Point of dilution
3'0"
7'0"
10'0"
2'1½"
#9
#10
#11
#12
Andersen Sampler
7'0"
6'0"
6'10"
19' 10"

PARTICULATE SAMPLING TUBE

Figure 4

The tube temperature profile during cycling sampling is shown in Table 6. Temperatures are in °F with the temperature range rather than average shown.

Table 6

DILUTION TUBE TEMPERATURE PROFILE DURING CYCLIC OPERATION SAMPLING

Run #	Cycle	TC #9	TC #10	TC #11	TC #12	Diluent Air
12	2	74-82	75-83	75-83	75-83	69-83
	3	83-97	84-97	83-91	83-94	69-83
	4	107-123	108-119	109-120	105-118	69-83
	5	81-112	81-112	80-111	80-112	69-83
14	2	79-85	76-85	76-85	76-85	78-82
	3	79-90	79-91	80-92	80-92	78-82
	4	115-120	113-119	117-123	116-123	78-82
	5	77-91	77-85	77-85	78-85	78-82
17	2	83-95	83-95	83-95	83-95	77-88
	3	89-110	88-105	88-106	88-106	77-88
	4	134-140	126-135	127-132	126-131	77-88
	5	90-103	87-101	86-101	90-101	77-88

2. Flow Rate/Volume, Dilution Ratio

Sample runs have been made with sampling into the tube at both steady-state (60 MPH road load) and under cycling conditions as per the cycling sequence described earlier. Flow rates and dilution ratios for all steady-state runs are shown in Table 7. Exhaust volume is calculated on the basis of fuel flow rates, air-fuel ratio, and C-H ratio of the fuel. These values are for mixed stream condition at the sampling zone temperature.

Table 7
DILUTION TUBE FLOW RATE AND DILUTION RATIO

Run #	Flow Rate cfm	Average Dilution Ratio (Air to Exhaust, Sampling Zone)
3	6.32	12.5:1
4	6.30	11.4:1
5	6.46	11.7:1
6	6.46	11.9:1
7	6.62	12.2:1
8	6.65	11.9:1
9	6.64	12.1:1
11	6.62	11.8:1
13	6.63	12.4:1
16	6.67	11.6:1

Cycling operation resulted in the following dilution tube conditions:

Table 8
DILUTION TUBE FLOW VOLUME AND FLOW RATE

Run #	Cycle	Flow Volume cfm	Flow Rate fps
12	2	538.9	6.85
	3	534.9	6.80
	4	530.0	6.74
	5	533.1	6.78
14	2	522.7	6.77
	3	544.7	6.93
	4	520.7	6.63
	5	550.0	7.0

Table 9

DILUTION TUBE SAMPLING ZONE TEMPERATURE FLOW RATE PROFILE

Vertical Probe			Horizontal Probe	
Air Flow (fpm)	Temp. °F		Air Flow (fpm)	Temp. °F
410	170	2"	385	168
410	170	3"	385	170
410	171	4"	390	171
405	171	5"	390	171
400	171	6"	405	171
400	171	7"	400	172
400	171	8"	395	172
400	171	9"	390	172
395	170	10"	400	172
400	170	11"	400	172
405	169	12"	405	171
380	167	13"	410	171
390	167	14"	420	169

Temperature Range	Vertical Profile:	167-171°F	2.2%
	Horizontal Profile:	168-172°F	2.2%
	TOTAL	167-172°F	2.9%
Flow Rate Range	Vertical Profile:	380-410 Units	7.9%
	Horizontal Profile:	385-420 Units	9.0%
	TOTAL	380-420	10 %

Stated accuracy of the air flow devices used is ±5% which should be considered in the 10% spread noted above.

The following table reflects the total particulate sample weight in grams collected by each Andersen Sampler for all sample runs at 1 cubic foot per minute flow rate which indicates the practical homogeneity of the air-exhaust mixture in the sampling zone.

Table 10
ACTUAL SAMPLE WEIGHTS FROM EACH ANDERSEN SAMPLER

Run #	B	C	D	Remarks
3	.0420	.0399	---	24 hours
4	---	.1215	.0988	48 hours
5	---	.0011	.0015	"
6	.0481	.0427	.0417	"
7	.0825	.0638	.0781	"
8	.1868	.1923	.1836	"
9	.1060	.0950	.0858	"
11	.1301	.1191	.1117	"
12	.0999	.1032	.1006	" , cycled
13	.0727	.0704	.0606	"
14	.0402	.0419	.0396	" , cycled
16	.0053	.0077	.0088	"
17	.0095	.0080	.0043	" , cycled
[1]Diluent Air	---	.0088	.0059	"
[2]Diluent Air	.0007	.0006	.0005	75 hours

---

[1] Fiberglass filter assembly on dilution tube inlet
[2] Dri-Pak filter assembly

Calculations for each test run regarding particulate collected in the Andersen Samplers are based upon a simple average of these weights.

C. GASEOUS EMISSIONS

1. Hydrocarbons

Unburned hydrocarbons are measured for engine cycles 2, 3, 4, and 5 during the 75 hour conditioning sequence with each test fuel by the method described earlier in the Exhaust Gas Analysis Section. Figures 5 through 17 indicate the effect of the conditioning sequence on exhaust hydrocarbons presented as parts per million, mole percent for all test fuels used in this study. The change during steady-state and cyclic sampling in the dilution tube is also shown.

Figure 18 indicates the percentage increase in exhaust unburned hydrocarbon emissions for the simple average of cycles 2, 3, 4, and 5 at 0 hours and at 75 hours, after the engine conditioning sequence. For example, in Run #3 (Indolene HO 30 fuel) the unburned hydrocarbons as an average of cycles 2, 3, 4, and 5 at 75 hours, increased 76% above the 0 hour (clean engine) average emissions for these cycles.

2. Nitrogen Oxide

Figure 19 represents the average change in nitrogen oxide (NO) emissions in the exhaust for engine cycles 2, 3, 4, and 5 as a result of the conditioning sequence of 75 hours. This data represent the increase (or decrease) in NO emissions from clean engine to fully conditioned engine (75 hours cycling) on each respective test fuel.

NO. 341-5½ DIETZGEN GRAPH PAPER
5 X 5 PER HALF INCH
EUGENE DIETZGEN CO.
MADE IN U. S. A.

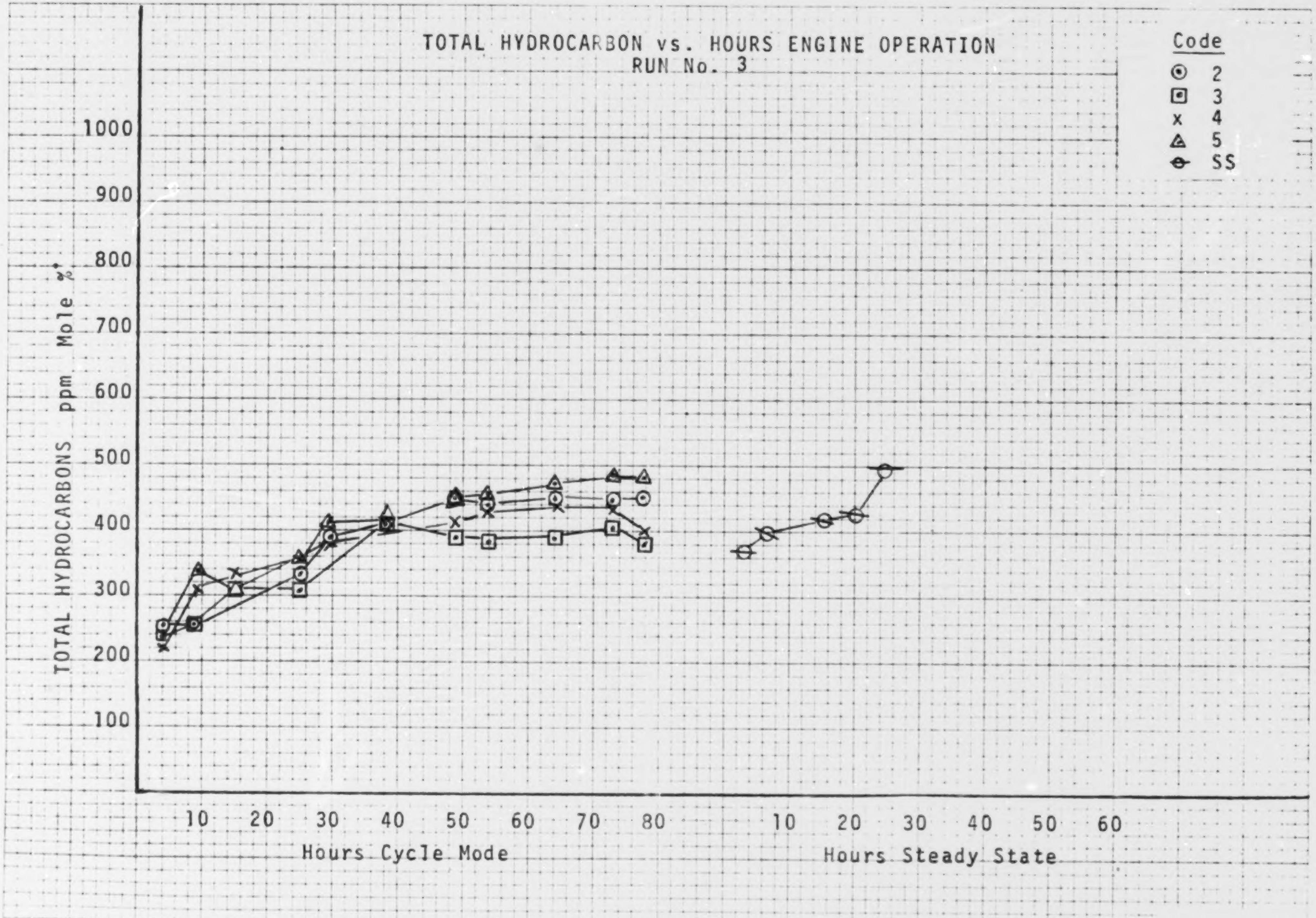


Figure 5

NO. 341-5½ DIETZGEN GRAPH PAPER
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EUGENE DIETZGEN CO.
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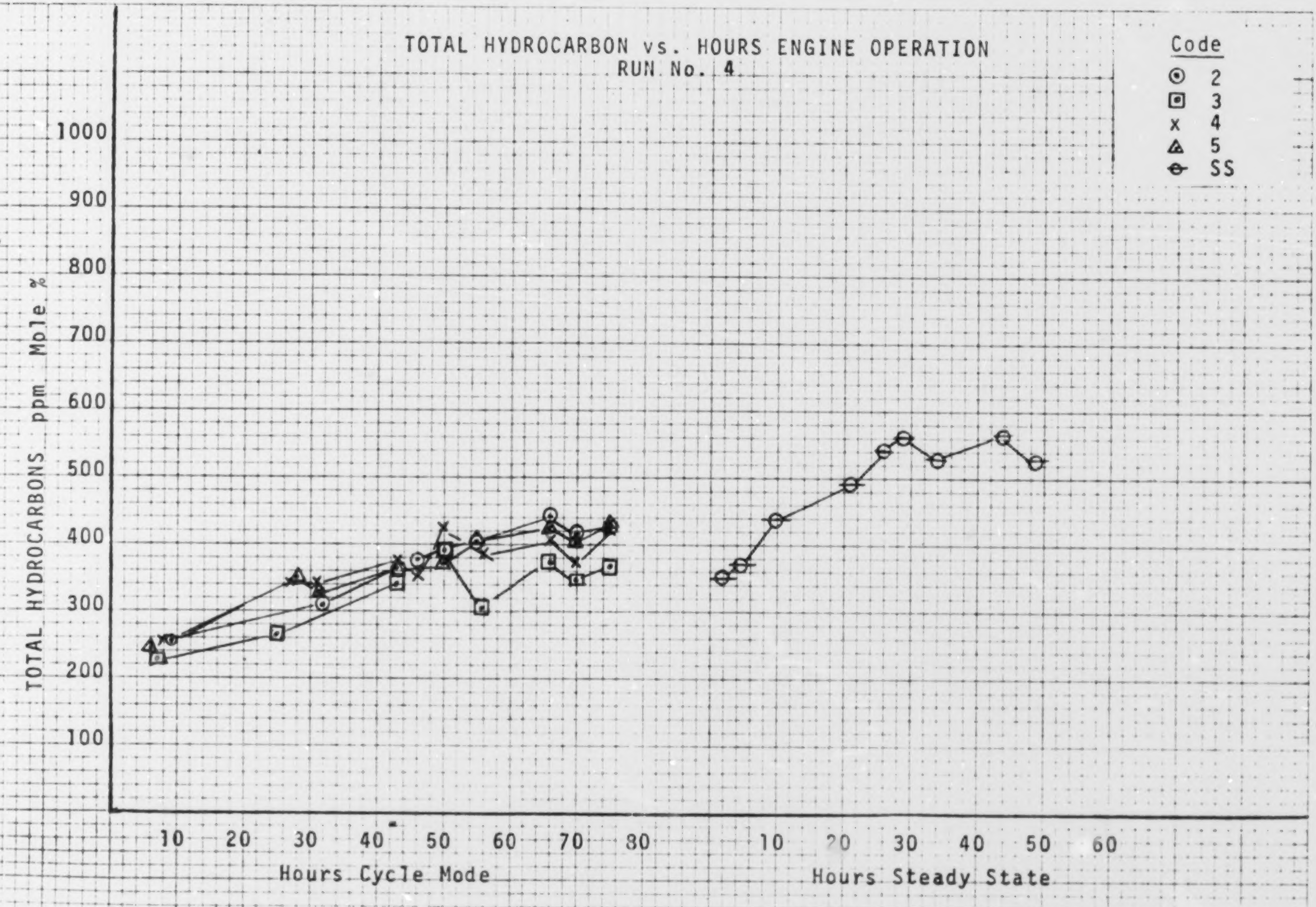

Figure 6

NO. 341-5½ DIETZGEN GRAPH PAPER
5 X 5 PER HALF INCH

EUGENE DIETZGEN CO.
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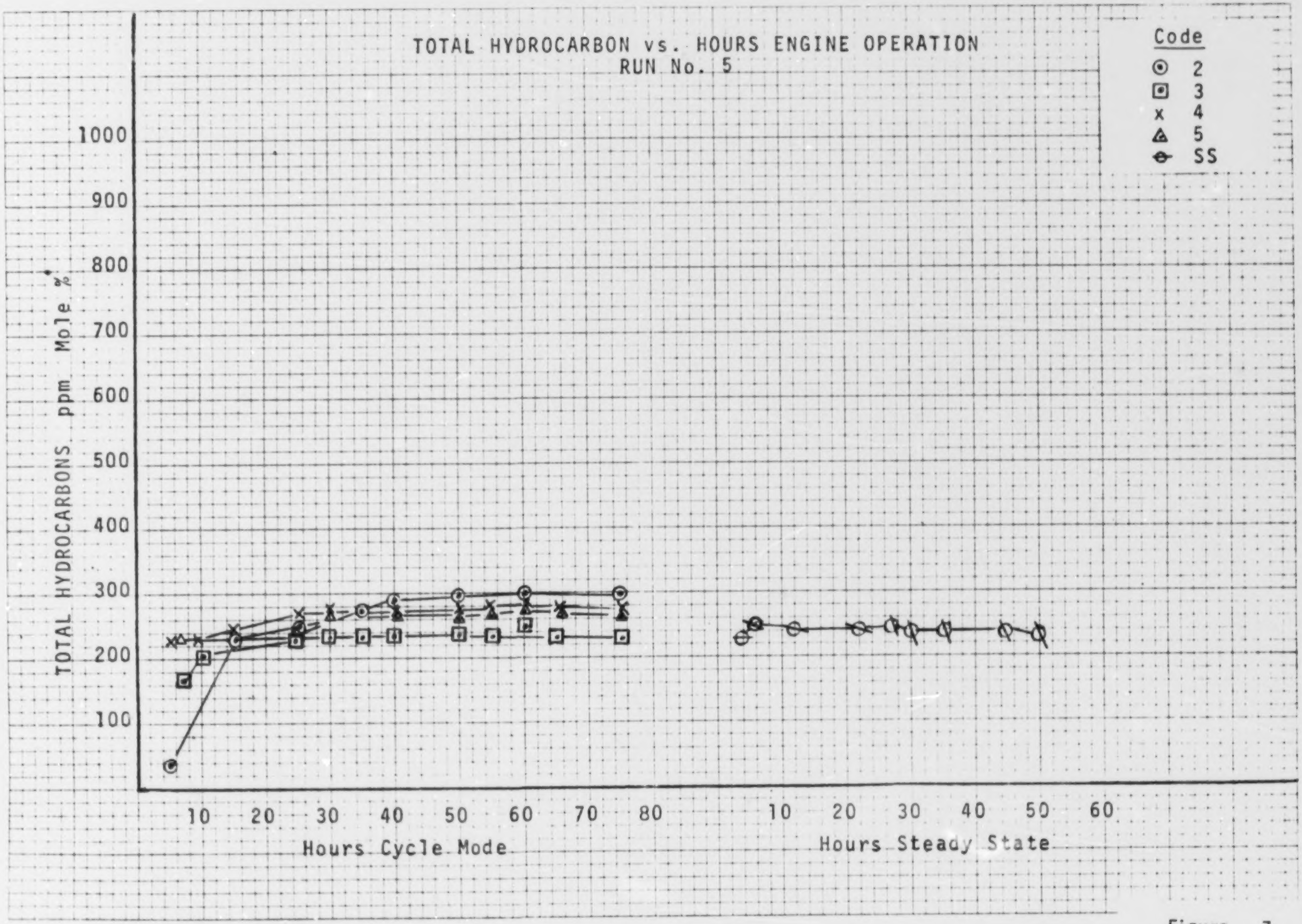

Figure 7

NO. 341-5½ DIETZGEN GRAPH PAPER
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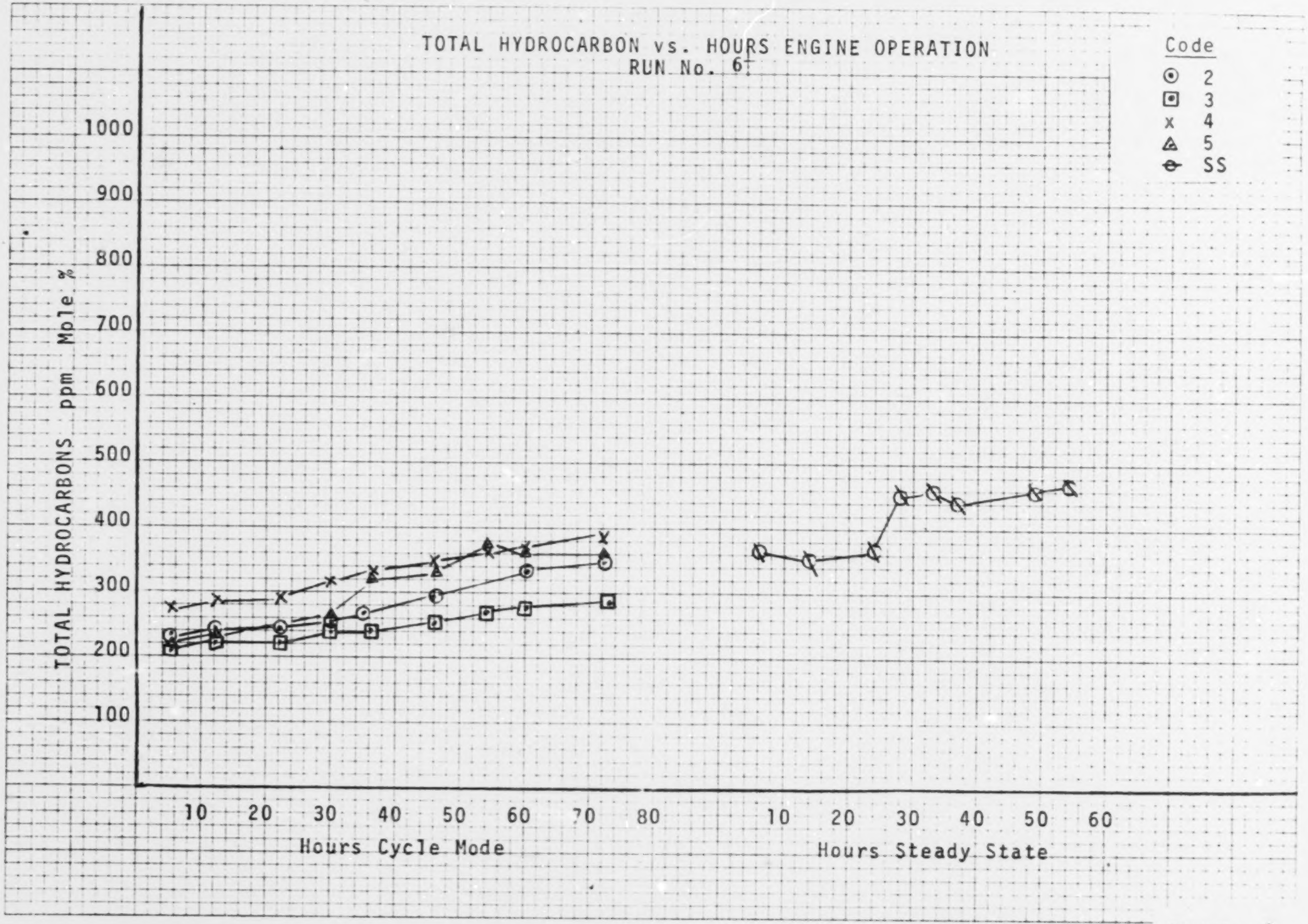

Figure 8

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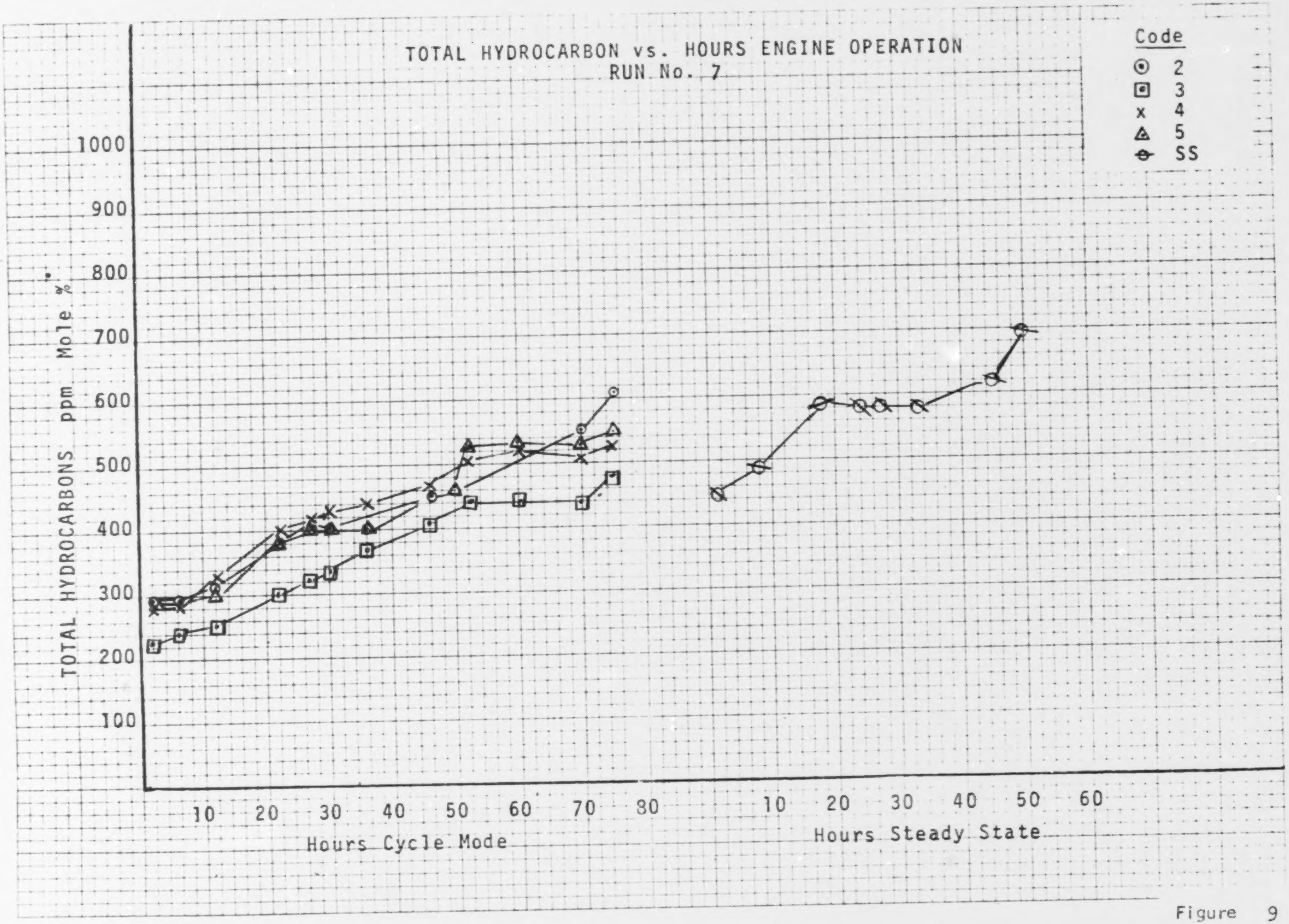

Figure 9

NO. 341-5½ DIETZGEN GRAPH PAPER
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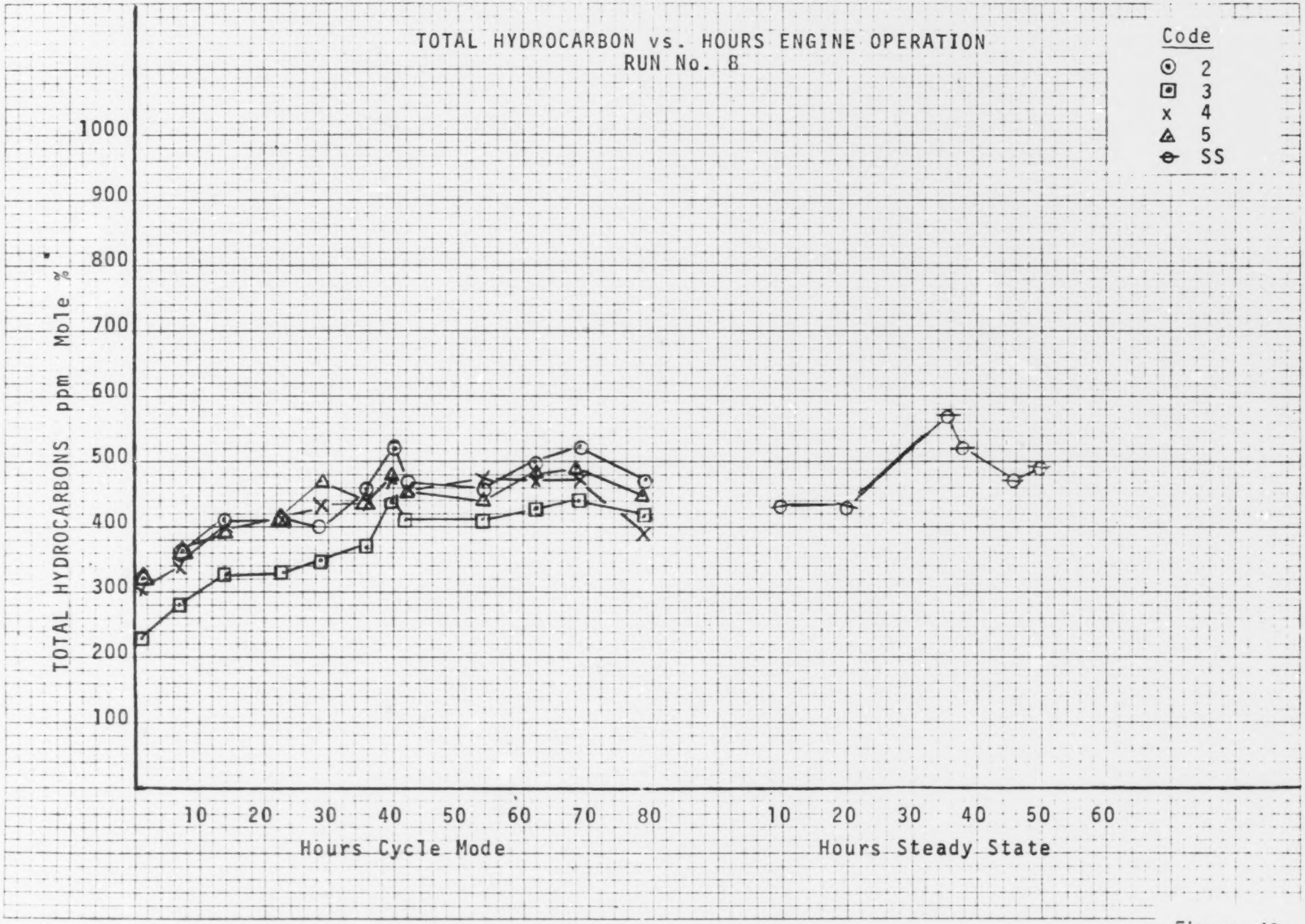
TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 8

Figure 10

NO. 341-5½ DIETZGEN GRAPH PAPER
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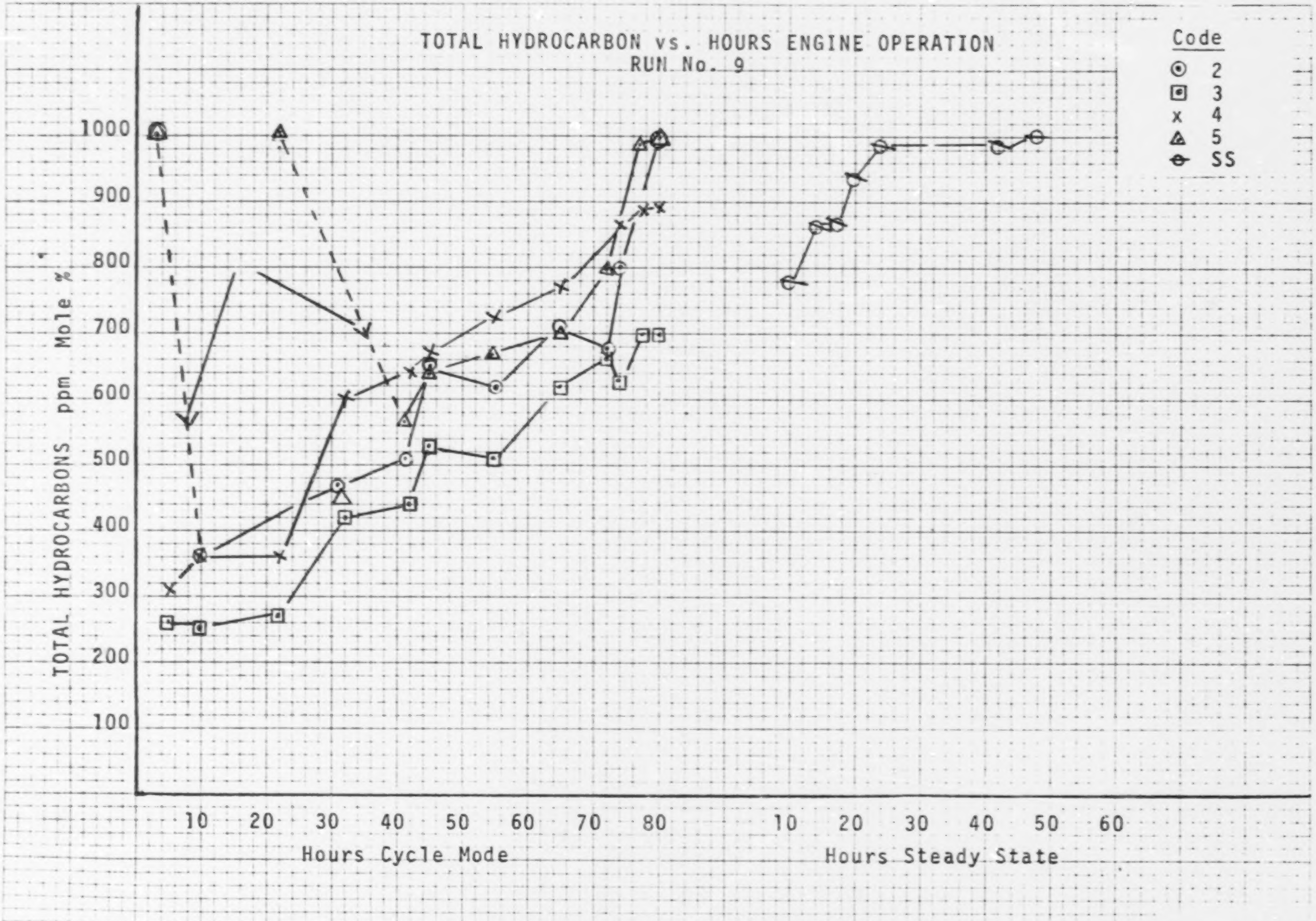
EUGENE DIETZGEN CO.
MADE IN U. S. A.

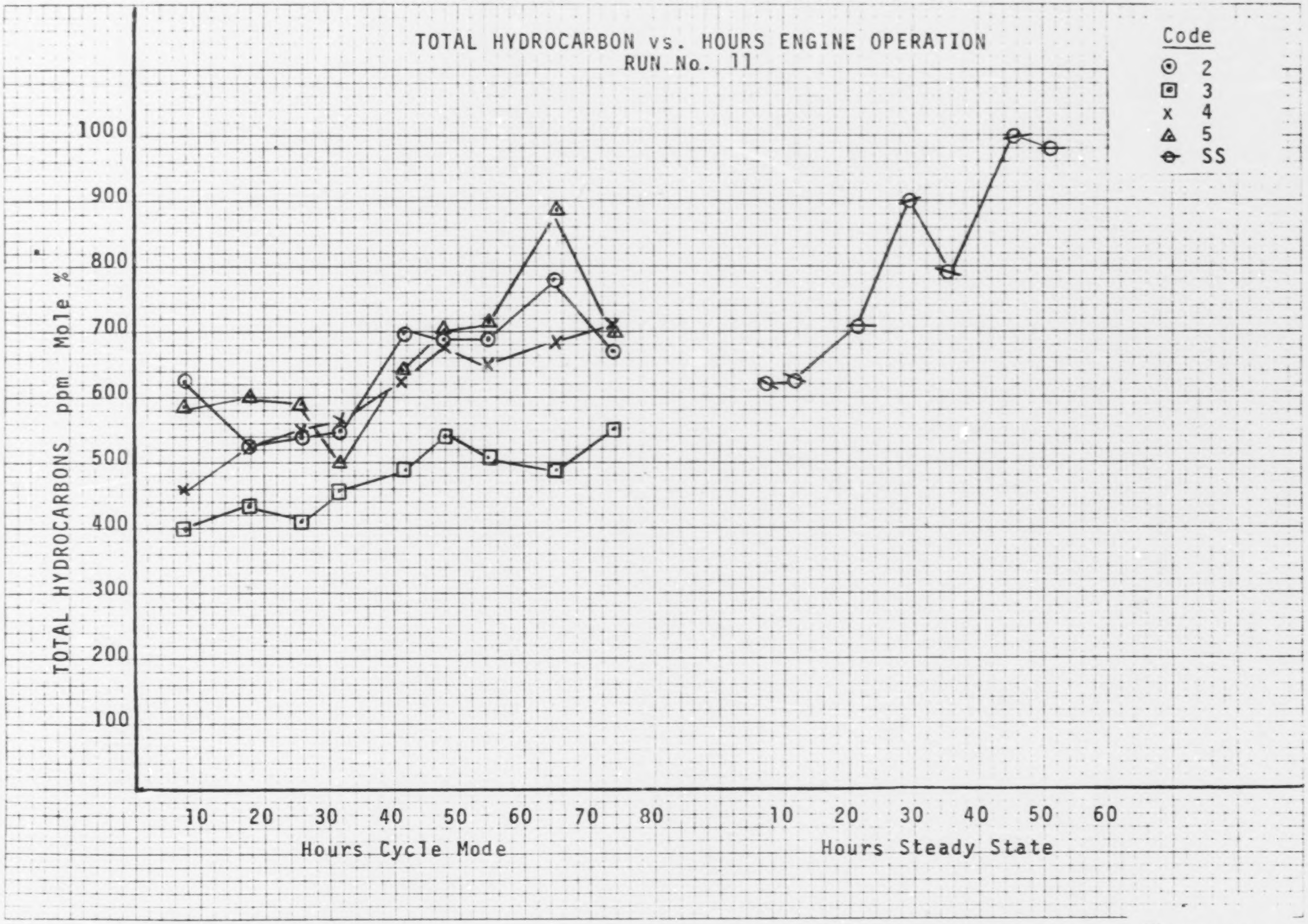


TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 9

Figure 11

NO. 341-5½ DIETZGEN GRAPH PAPER
5 X 5 PER HALF INCH

EUGENE DIETZGEN CO.
MADE IN U. S. A.



TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 11

Figure 12

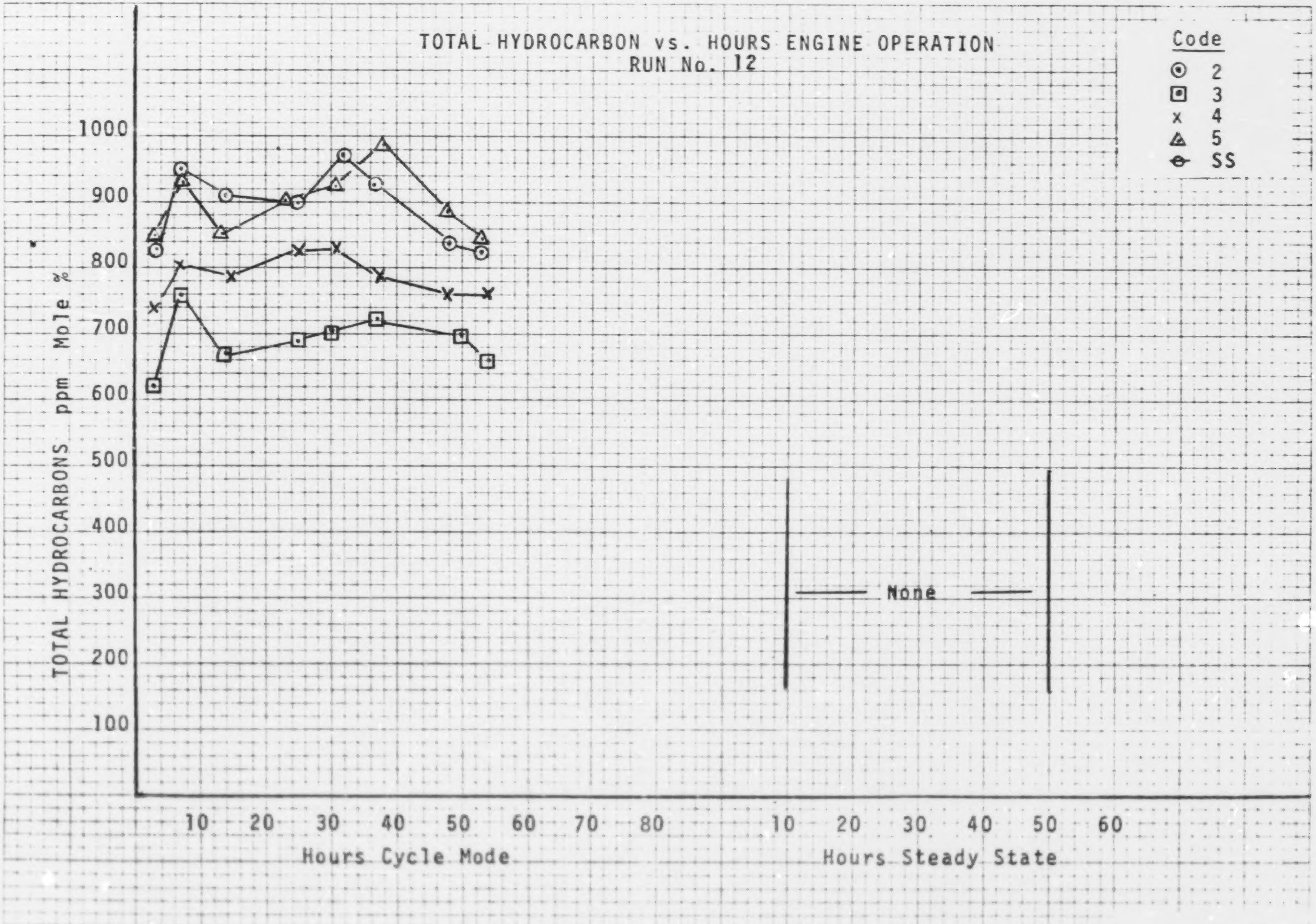
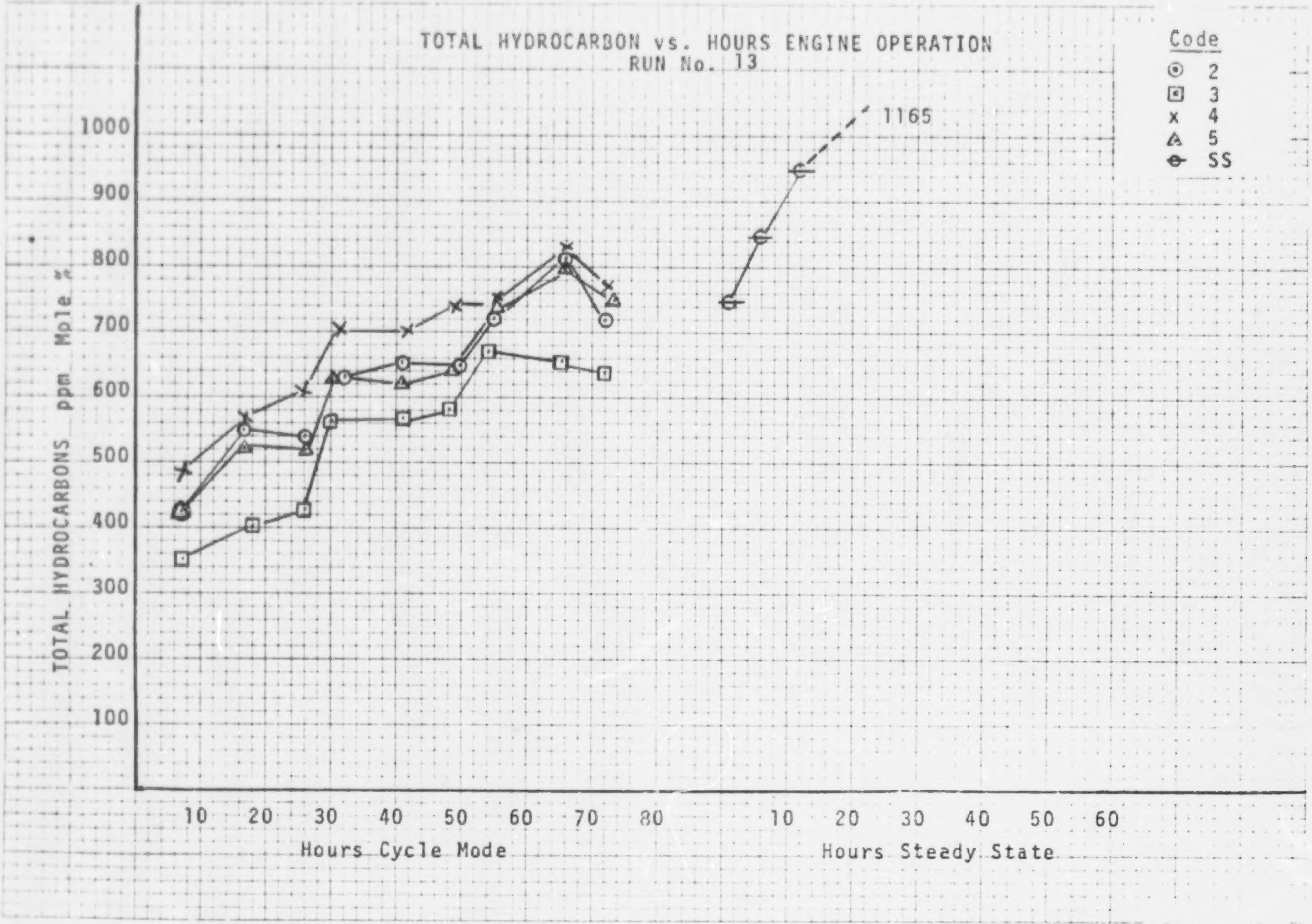

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 12
Code
⊙ 2
⊡ 3
x 4
△ 5
⊖ SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State
None

Figure 13

NO. 341-5½ DIETZGEN GRAPH PAPER
5 X 5 PER HALF INCH
EUGENE DIETZGEN CO.
MADE IN U.S.A.



TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 13

Figure 14

NO. 341-5½ DIETZGEN GRAPH PAPER
5 X 5 PER HALF INCH

EUGENE DIETZGEN CO.
MADE IN U. S. A.

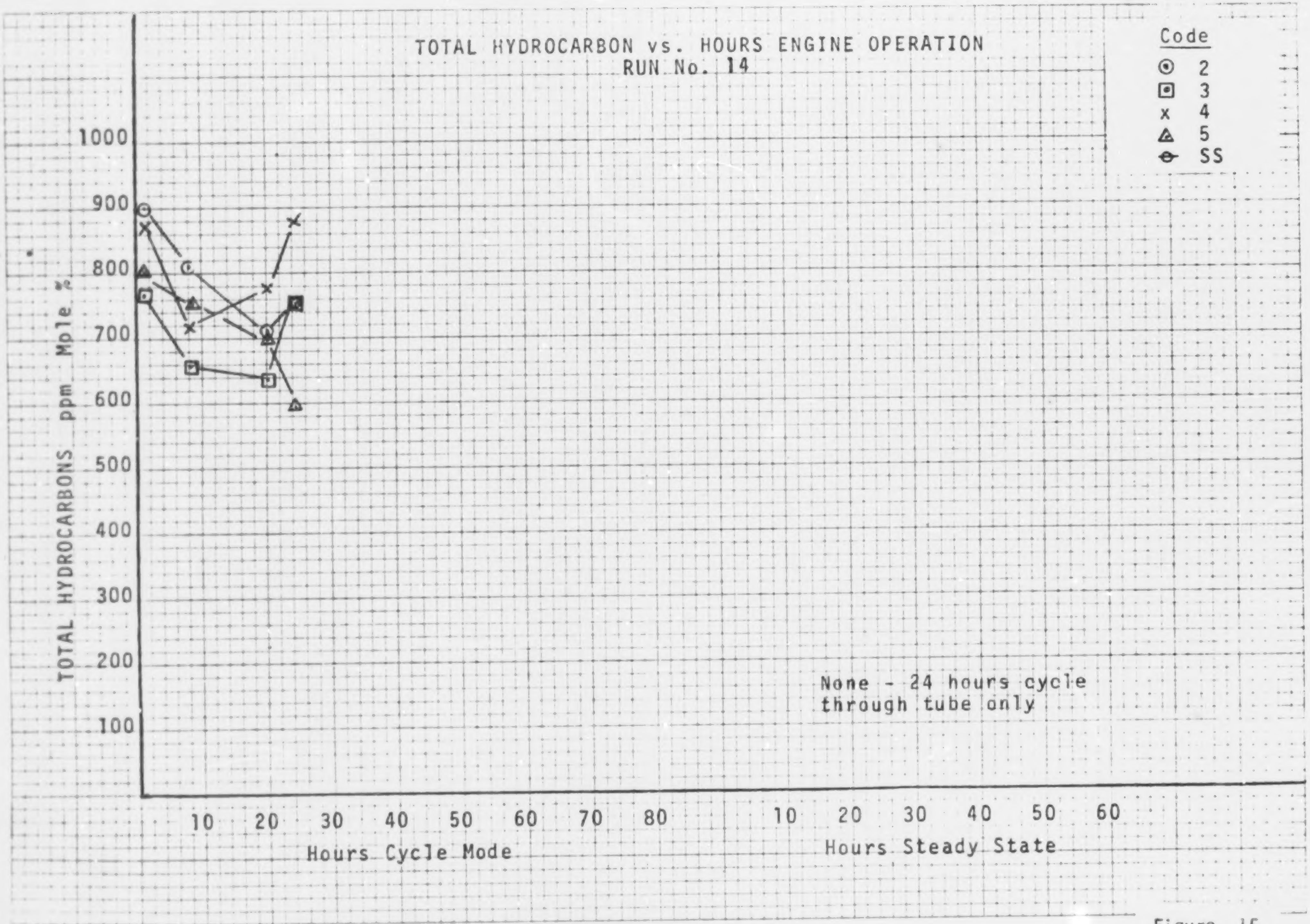


Figure 15

NO. 341-5½ DIETZGEN GRAPH PAPER
5 X 5 PER HALF INCH
EUGENE DIETZGEN CO.
MADE IN U. S. A.

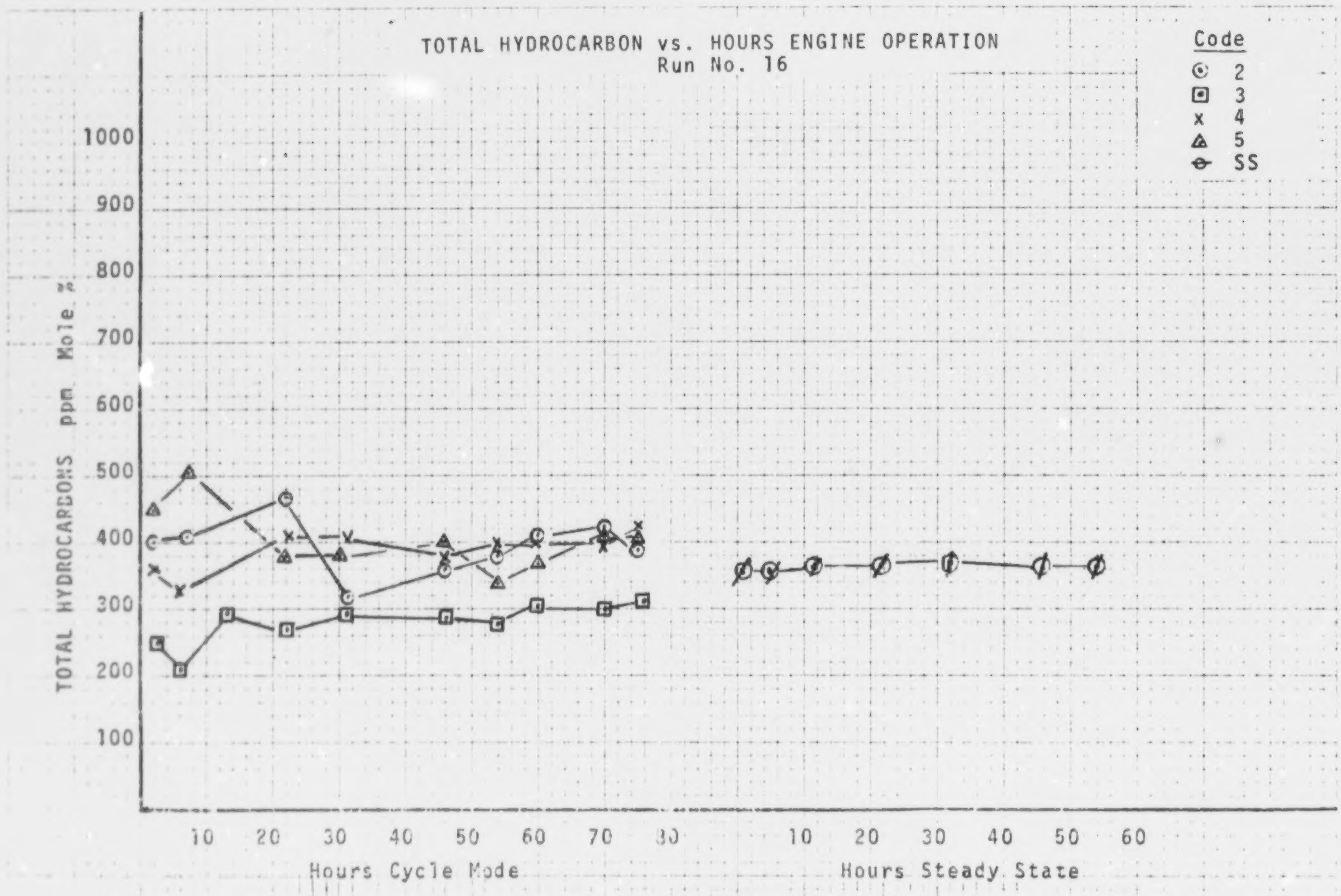


Figure 16

NO. 341-5½ DIETZGEN GRAPH PAPER
5 X 5 PER HALF INCH

EUGENE DIETZGEN CO.
MADE IN U. S. A.

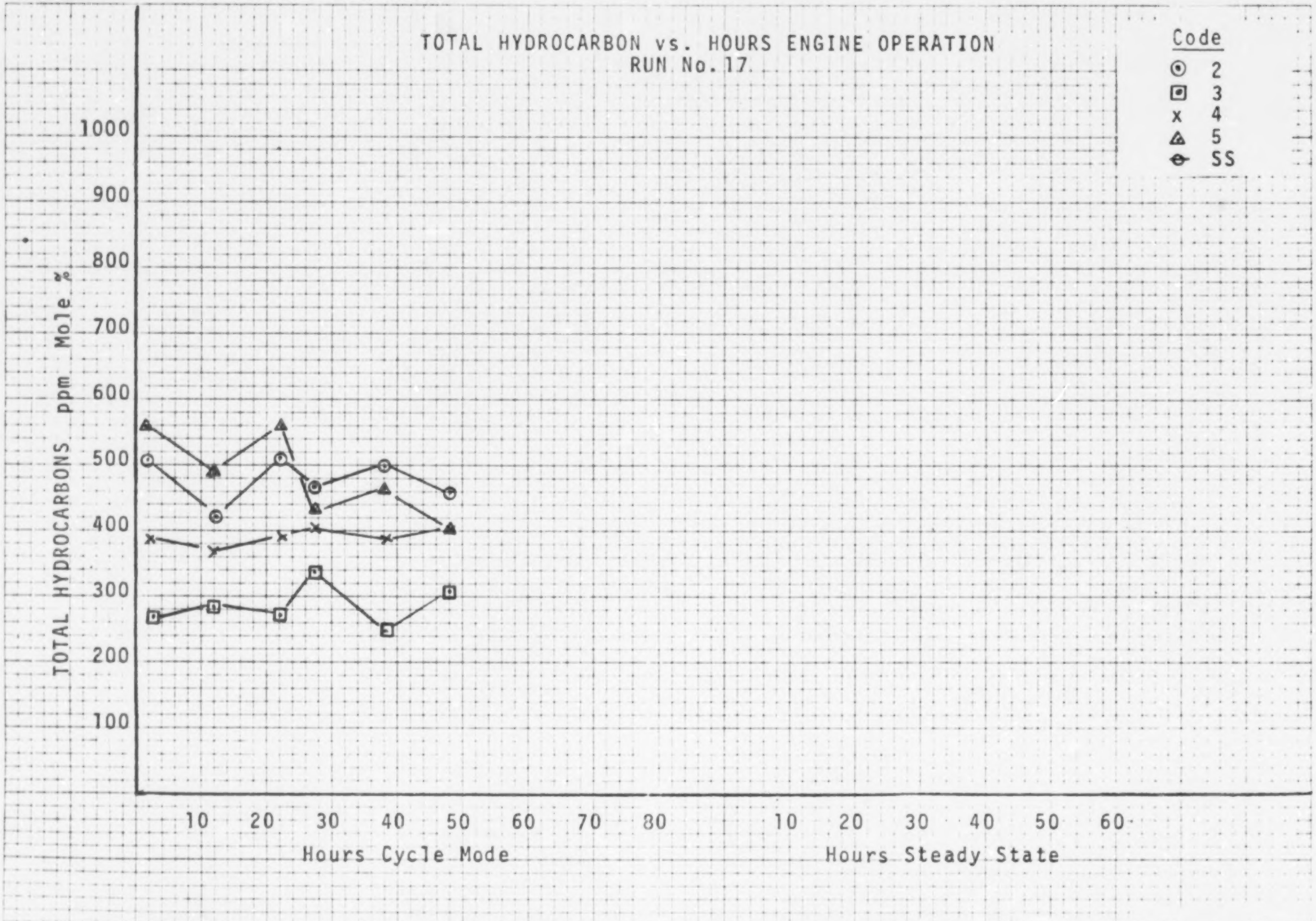


Figure 17

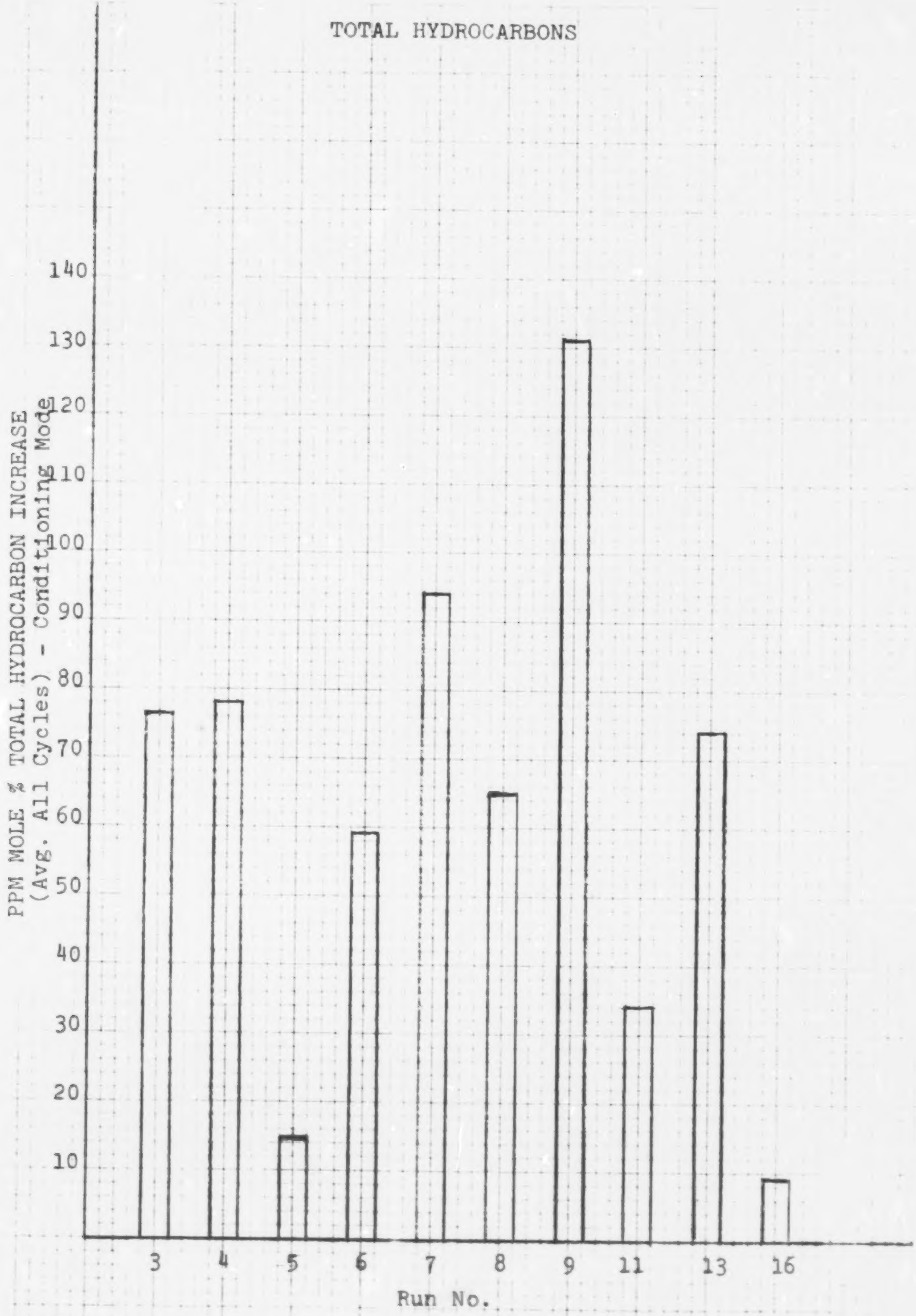

TOTAL HYDROCARBONS
PPM MOLE % TOTAL HYDROCARBON INCREASE
(Avg. All Cycles) - Conditioning Mode
140
130
120
110
100
90
80
70
60
50
40
30
20
10
3
4
5
6
7
8
9
11
13
16
Run No.

Figure 18

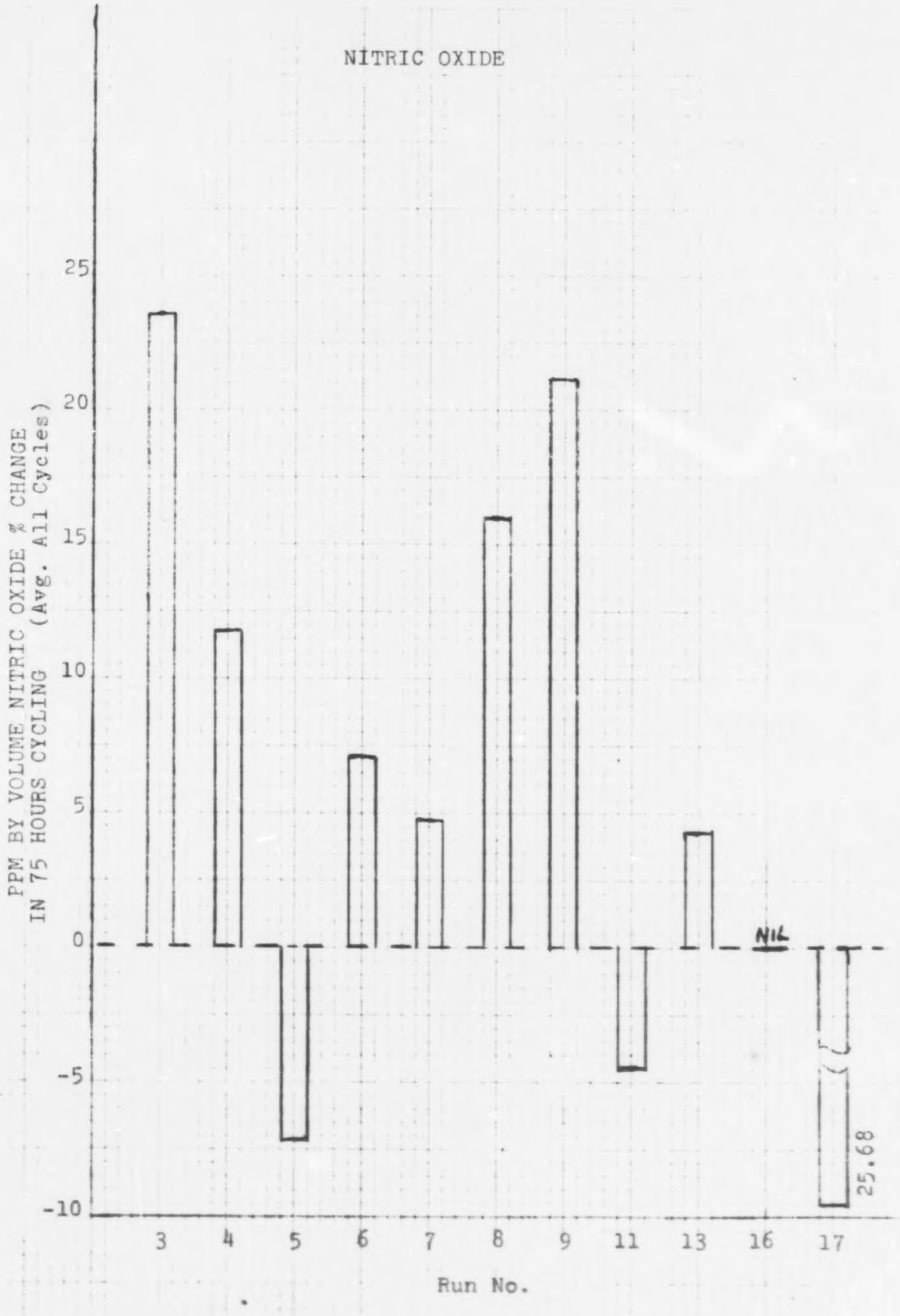

NITRIC OXIDE
PPM BY VOLUME NITRIC OXIDE % CHANGE
IN 75 HOURS CYCLING (Avg. All Cycles)
25
20
15
10
5
0
-5
-10
NIL
25.68
3
4
5
6
7
8
9
11
13
16
17
Run No.

Figure 19

D. FUEL ANALYSIS

The following is the physical analysis of test fuels used in these studies:

Table 11

PHYSICAL ANALYSIS OF TEST FUELS

	Indolene HO	Indolene HO 15	Indolene* HO 30	Indolene HO+ 3cc TEL/Gal.	Indolene** HO 30
Distillation D86, °F					
IBP	100	88	92	90	90
5	126	118	118	116	118
10	140	137	132	130	133
20	165	166	162	159	162
30	190	190	190	190	188
40	207	207	207	202	208
50	221	220	218	220	222
60	231	236	238	235	234
70	244	249	250	249	249
80	268	272	274	274	273
90	320	332	326	328	320
95	368	386	364	370	368
E.P.	395	398	404	394	394
% Recovery	96.5	96.0	97	96	96.5
% Residue	0.6	0.6	0.6	0.4	0.5
% Loss	2.9	3.4	2.4	3.6	3.0
RVP	7.3	7.4	8.2	8.5	---
Octanes:					
MON	87.5	92.3	96.3	95.6	95.9
RON	97.4	101.2	103.4	103.2	102.9
FIA:					
% Saturates	66.4	63.1	65.9	65.1	68.1
% Olefins	4.2	4.6	3.6	3.2	3.0
% Aromatics	29.4	32.3	30.5	31.7	28.9
cc/gal TEL	0.06	1.5	3.0	3.0	3.0

---

* 1st load Indolene HO 30 Fuel

** 2nd load Indolene HO 30 Fuel (Run #11, on)

These are the base fuels for all runs reported. Individual physical analysis of each additional test fuel was, therefore, not conducted. Analysis of each fuel was conducted to verify concentration of additives being used, however.

Trace metal analysis of the 2nd batch of Indolene HO 30 fuel is shown below:

Table 12

TRACE METAL ANALYSIS OF INDOLENE HO 30 FUEL

Fe	<1.0 ppm
Ni	<0.5 ppm
Cu	<0.2 ppm
Mg	<0.5 ppm
Zn	<3 ppm
Al	<1.0 ppm
Ca	<1.0 ppm
Mn	<1.0 ppm
Sb	<1.0 ppm
Ti	<1.0 ppm

The weight percentage of carbon (C) and hydrogen (H) in several of the test fuels was determined by an automated Pregl microanalysis combustion technique. The fuel is first pyrolized in argon to avoid explosion hazard. Results are shown in Table 13 and were used for exhaust gas volume calculations.

Table 13

WEIGHT PERCENTAGE CARBON (C) AND HYDROGEN (H) IN SEVERAL TEST FUELS

Fuel	Wt. % C	Wt. % H
Indolene HO 30	86.4, 86.3	13.19, 12.99
Indolene HO 15	85.7, 85.9	13.11, 13.07
Indolene HO 0	86.3, 86.2	13.28, 12.91
Indolene HO 0 + 3 ml TEL/gal.	86.4, 86.1	13.26, 13.31

As these are basic fuels used for all runs reported, this analysis was not repeated for each specific test run fuel mix.

E. ENGINE OIL TRACE METAL ANALYSIS

The following table shows results of trace metal analysis on new and used Amoco 100 SAE 30 motor oil used in all tests reported herein. Analysis is by Emission Spectroscopy and results are reported in weight percent.

Table 14

TRACE METAL ANALYSIS OF NEW AND USED ENGINE OIL

Element	Amoco 100 New	Run #5* Oil Filter	Run #13** Oil Filter	Run #13** Crankcase
Fe	.0002 wt. %	.012 wt. %	.012 wt. %	.012 wt. %
Ni	<.0001	<.0005	<.0005	<.0005
Cu	<.00002	.0003	.0002	.0002
Al	.0001	<.0005	.0013	.0012
Ca	.0017	.0057	.0028	.0026
Si	.0001	<.0005	.0010	.0030
Mg	.089	.083	.084	.088
Mn	.0001	<.0005	<.0005	<.0005
Pb	.0006	.12	1.3	1.3
Cr	<.0001	.0008	.0055	.0048
Sn	<.0001	<.0005	<.0005	<.0005
Zn	.081	.078	.082	.076
Ti	<.0001	<.0005	<.0005	<.0005
P	.05	<.1	<.3	<.3
Mo	<.0001	<.0001	.0012	.0011

---

*Indolene HO Fuel
**Indolene HO 30 Fuel

F. ENGINE COMBUSTION CHAMBER DEPOSITS

Total combustion chamber deposits from all cylinders of the test engine for all sample runs are shown in Figure 20. Runs 11, 13, and 16 are not shown as runs 12, 14, and 17 were made directly after these runs without cleaning or re-conditioning the engine. Deposits are shown in grams. Each run is of somewhat different duration notably those such as run 11/12 where steady-state and cycling sampling runs are conducted. Total engine hours for each run are shown at the top of each data bar.

Combustion chamber deposit analyses for these runs are shown in Table 15:

Table 15

ENGINE COMBUSTION CHAMBER DEPOSIT ANALYSIS

Run #	Wt. % Pb	Wt. % Fe	Wt. % C	Wt. % Br	Wt. % Cl
4	64.6	0.26	5.7	8.21	10.81
5	5.9	1.1	55.9	0.55	0.57
6	54.9	0.27	12.0	8.19	9.78
7	72.0	0.2	11.0	0.6	0.28
8	59.8	.18	7.8	20.67	0.58
9	67.9	.217	7.4	0.55	13.55
12	66.4	.177	6.01	9.10	8.99
14	65.6	.190	6.08	9.12	9.85

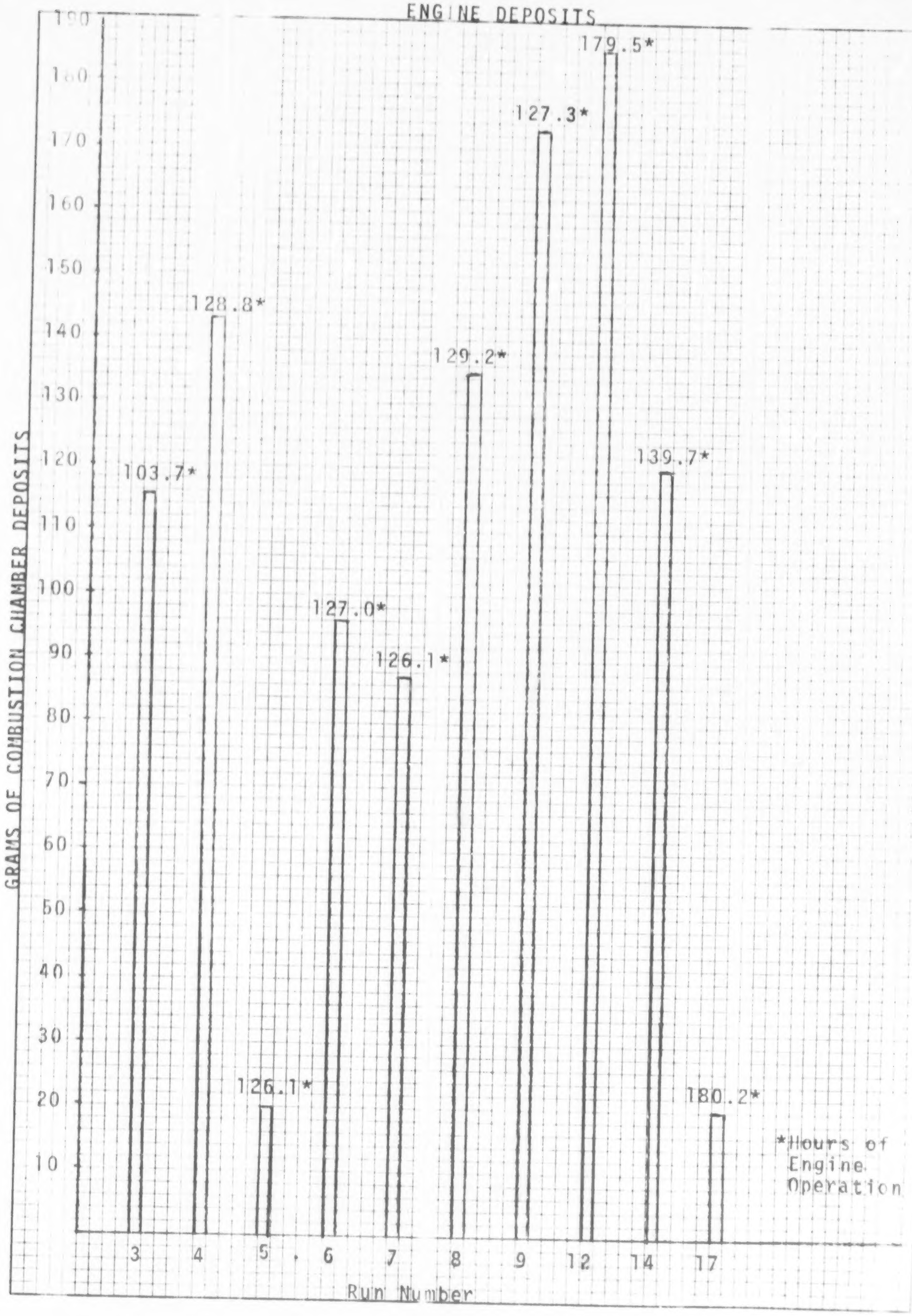


Figure 20

K&E 10 X 10 TO THE INCH 46 0663
7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

G. MICROSCOPY (P. Traylor)

1. Introduction

The responsibility of the Microscopy Laboratory is to apply light, transmission and scanning electron microscopies in characterization of the automotive exhaust particulates relative to:

1. Color
2. Size
3. Shape, Form
4. Fusion Characteristics
    (a) Melting point
    (b) Sublimation
    (c) Crystallinity
5. Electron Diffraction
6. Solubility
7. Organic-inorganic Composition
8. Elemental analysis by X-ray fluorescence while in the scanning electron microscope.

The plan of attack up to this point for the Microscopy group included the development of sampling techniques for the characterization work, developing characterization techniques and skills, making characterizations, and establishing the most useful parameters for future work. The immediate goal was to become well acquainted with the exhaust particle as rapidly as possible and be prepared to read out characteristic changes relative to changes in fuel composition and engine operating conditions.

The work on the exhaust particle was divided into four parts. Submitted here will be summary reports of what has been accomplished. Each summary report will contain either a copy of or examples of all routine laboratory reports submitted on the individual runs.

These summary reports deal primarily with the responsibilities mentioned above.

2. Scanning Electron Microscopy and X-Ray Fluorescence Analysis - (Lois Settlemeyer)

a. Purpose

To characterize (SEM) and identify (x-ray spectrometer) the particulates in exhaust emission collected by the Andersen Sampler or collected on the Millipore filter following the sampler.

b. Instrumentation

Cambridge Stereoscan Mark 2A
Ortec non-dispersive x-ray detector
Nuclear Data Analyzer
Varian Vacuum Evaporator
Kinney Vacuum Evaporator

c. Work Outline

1) Particle characterization (SEM) on plates 1, 3, and 6 of the Andersen Sampler.
2) Particle identification (x-ray).
3) Single element x-ray scan.
4) X-ray spectra on impingement area of plates 1, 3, and 6, and spectra on final filter.

d. Technique and Methods

1) Substrates - Initial sampling for the SEM was by breaking the glass collection plates used in the Andersen sampler. This was awkward and often resulted in loss of particulate. Because of this various substrata were attached to the Andersen collection plate with double adhesive tape. Micro cover glasses, mylar strips, epoxy with lamp black, and ultra pure carbon strips were tried. Most satisfactory were micro cover glasses, but the ultra pure carbon strips proved best where x-ray analysis was to be done. Silica interference from the micro cover slips, halogens in epoxy, and thermal instability in mylar film reduced their desirability for x-ray substratum.

2) Conditions for Andersen Sampler - The initial purpose of this analysis was to identify and characterize individual particles (1μ to 50μ). Sampling with the Andersen Sampler at a flow rate of 1/2 CFM yielded sufficient particulate for documentation and reduced breaking and piling as was evidenced at 1 CFM.

3) Storage and Sample Preparation - All samples were maintained in a dry atmosphere from collection to examination. Both the glass cover slip and the carbon strip were attached to SEM sample stubs with conducting silver paint. Samples for SEM characterization were made conductive with a thin layer (~ 200 Å) of gold or gold-palladium evaporated onto under vacuum (5×10^{-4} Torr). Graphite carbon was sputtered on the samples used for x-ray identification.

4) Normal Operation for the Stereoscan -
  a) Gun potential - 20 to 30 kv (depending on degrading of sample and resolution needed)
  b) Vacuum - $\sim 10^{-4}$ Torr maintained
  c) Sample angle - 20°
  d) Working distance - 11 mm
  e) Polaroid P/N Type 55 film with 100 sec. exposure

5) Normal Operations for X-Ray Detector (warranted 215 ev FWHM resolution)
  a) Gun potential - 30 kv
  b) 1024 channel - analog to digital converter
  c) Collection time - 200 sec.
  d) Count rate - ∼600 c.p.s.
  e) Spectra recorded on Moseley 7035B X-Y recorder
  f) Single channel recording
     Polaroid P/N Type 55 film
     400 sec or 800 sec. exposure depending on concentration

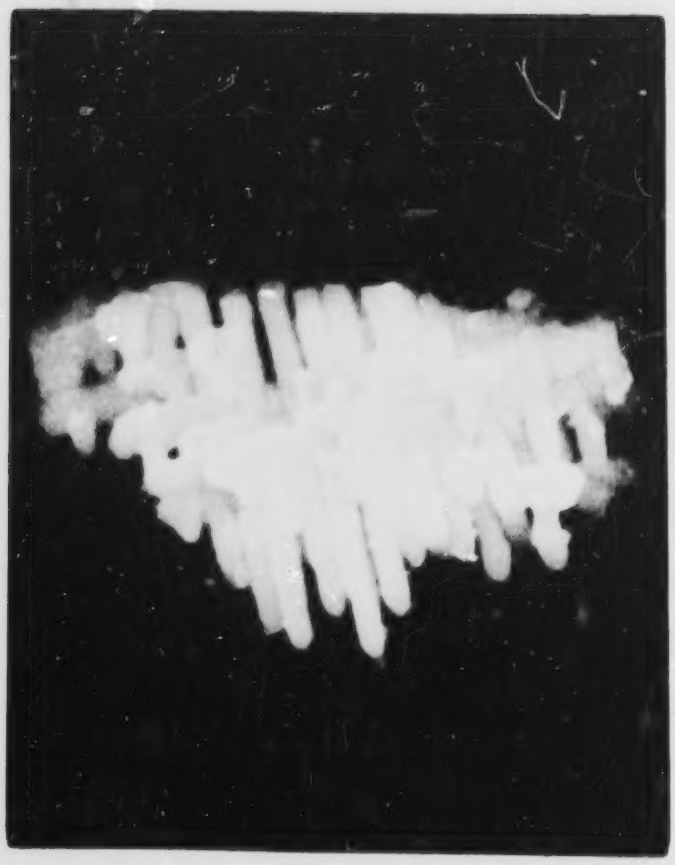
e. Results

1) Particle documentation - All particles were classified into basic groups (1) individual particle - one structural type >3μ (Figures 21, 22, and 23); (2) agglomerate - a single mass of <1μ particles (Figure 24-A); (3) fines - particles 500Å to 1000Å (Figure 25).

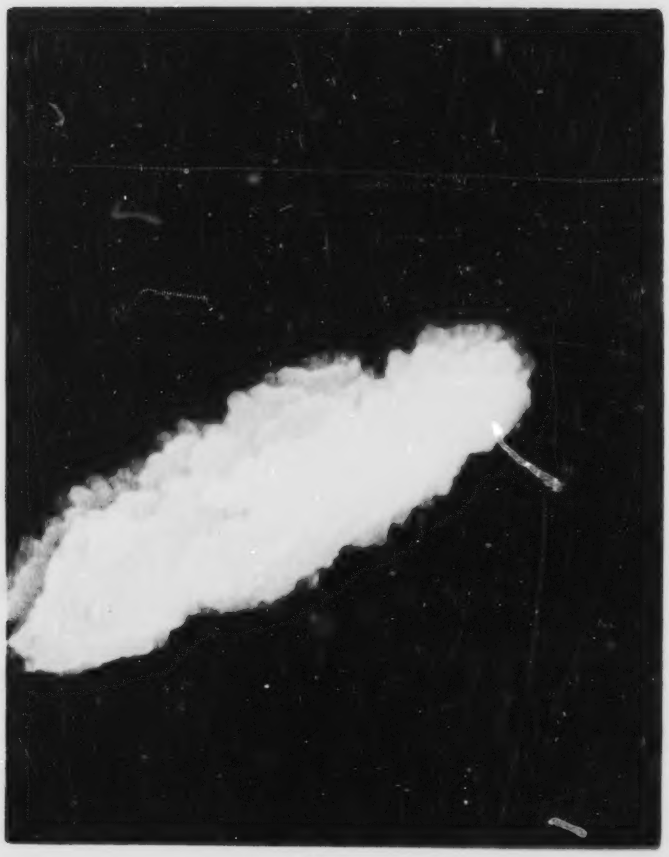
On each run, plate 1 and 3 consisted mainly of individual particles with an increasing amount of fines from plate 1 and plate 6. Agglomerates and heavy concentrations of fines were dominant on plate 6.

Figure 21

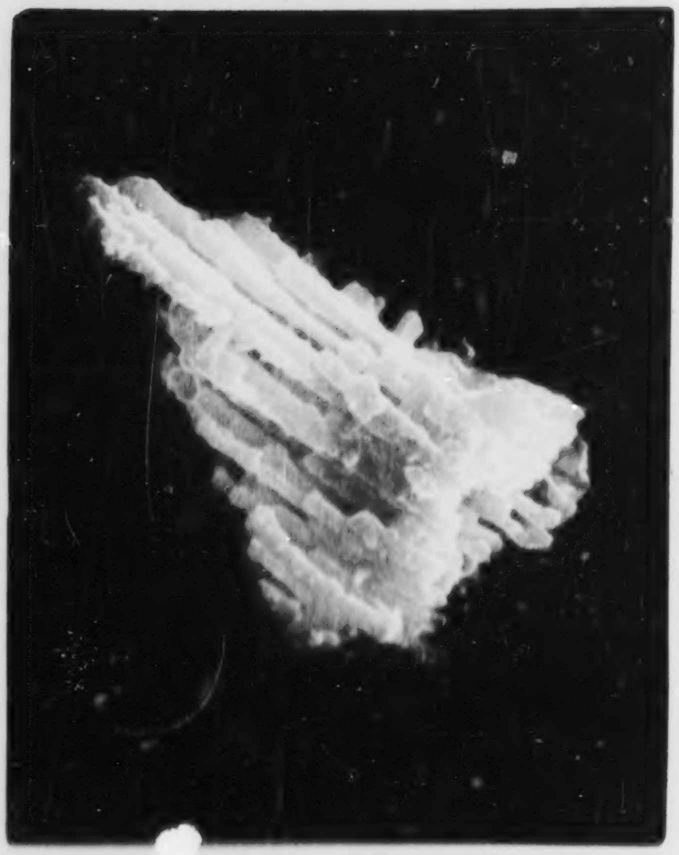
TYPICAL
INDIVIDUAL
PARTICLES



A

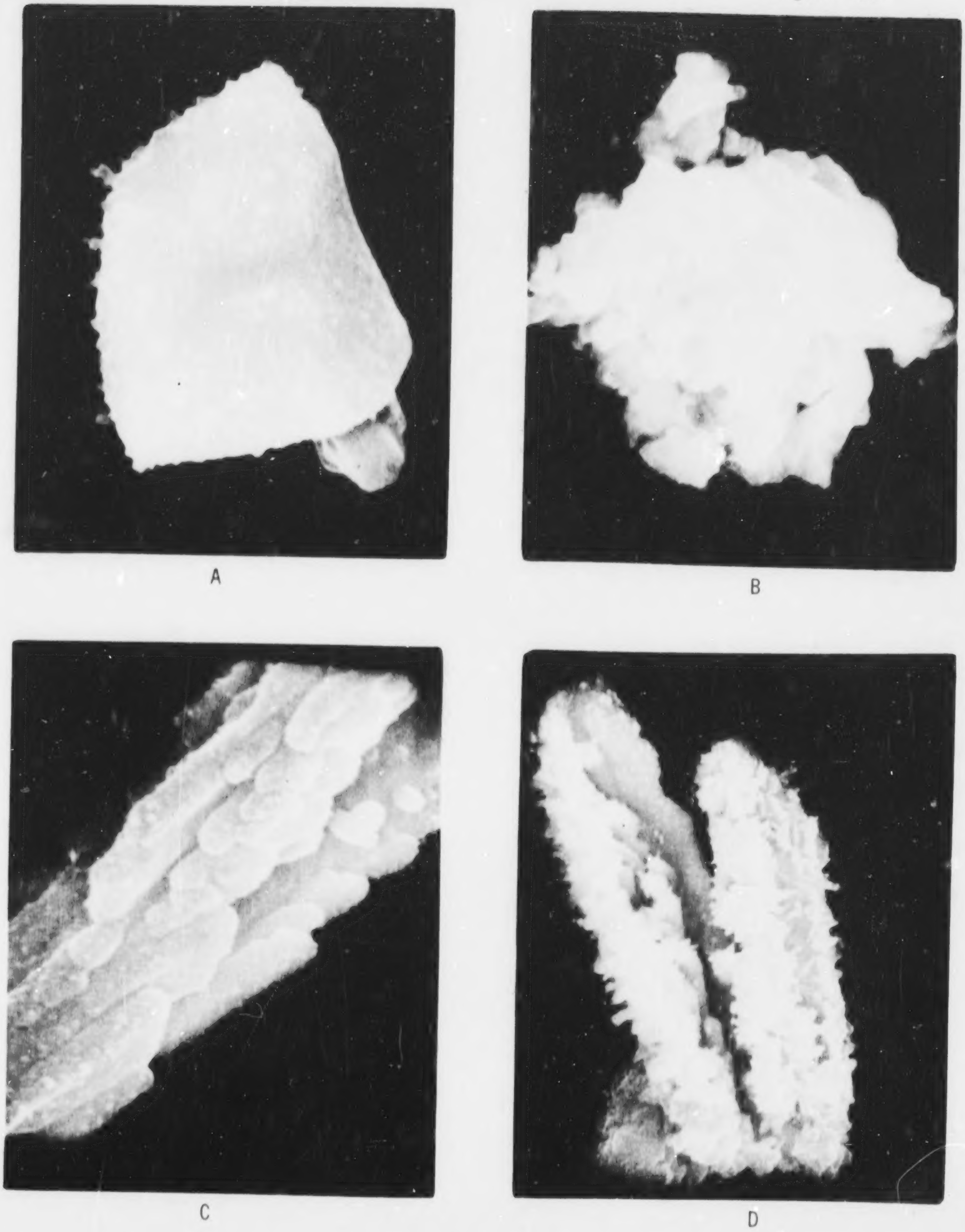


C



B

Figure 22



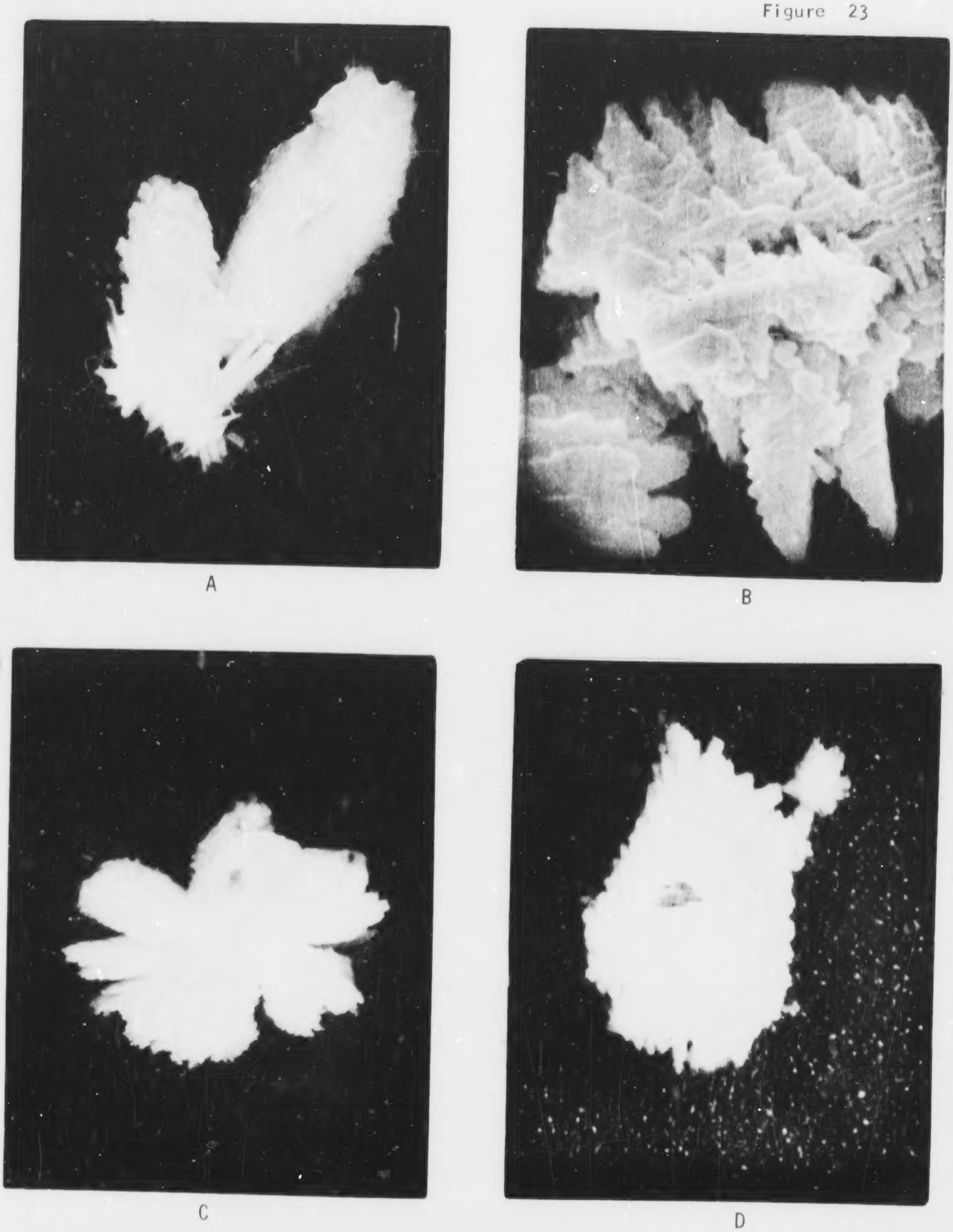
A

B

C

D

Figure 23



A

B

C

D

Figure 24

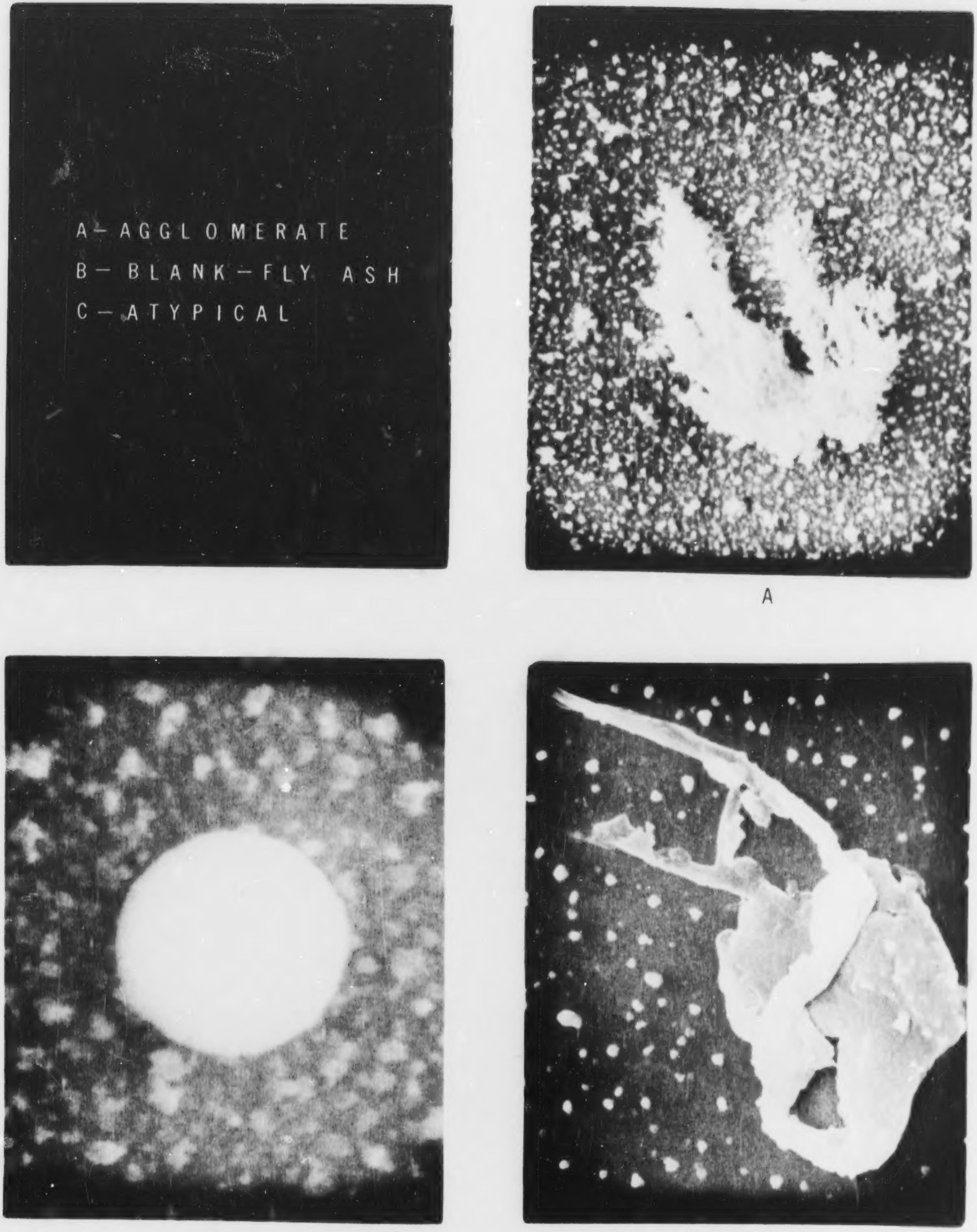
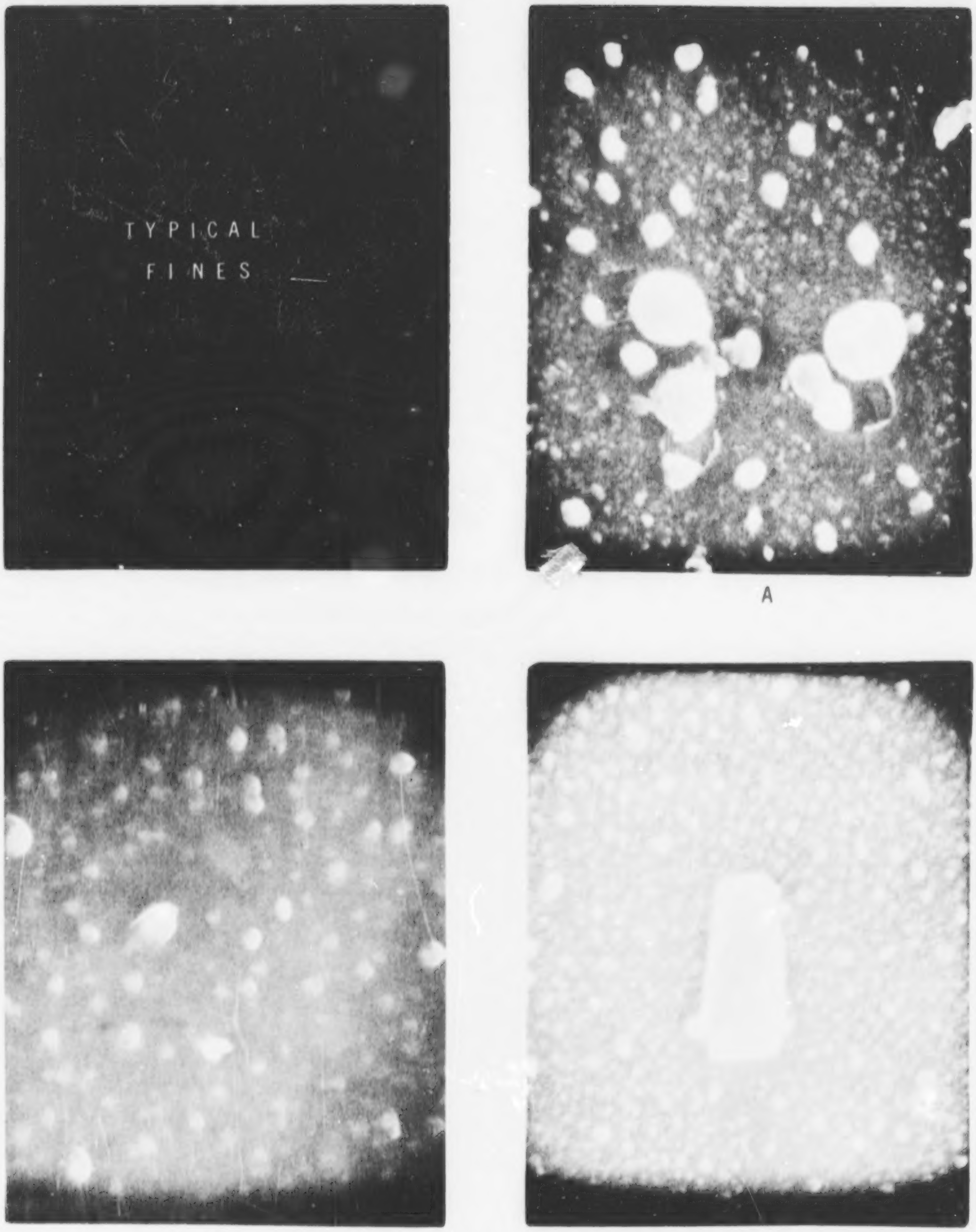

A—AGGLOMERATE
B—BLANK—FLY ASH
C—ATYPICAL
A
B
C

Figure 25


TYPICAL FINES

A

B

C

The fines from one run to another and from one tray to another differed significantly. Two possible reasons for this: 1) mass differences, 2) different substratum. In one case, fines collected equidistant from an impingement point, but on different substratum revealed different types of fines. Some of these fines, particularly runs #5 and #12, degrade under the beam indicating either the presence of organics or highly volatile inorganics.

2) Particle Identification (X-ray) - In most cases background and variations were observed. Characteristic of diluent blank runs (Figure 24) were particles high in iron. Several different particle shapes would yield Pb:Cl:Br and likewise some particles very similar in crystalline form would yield different spectra. Due to the M orbital of Pb being the same energy as the $K\alpha$ orbital of S, positive identification of sulfur in the presence of lead cannot be made. At present, no correlation between shape and chemical identification has been made.

3) Single Element X-ray Scan - This mode of operation allowed the presence or absence of a single element in a group of particles to be determined. The element most often scanned was lead. Individual particles most noticeably reduced in lead concentration were flat,

smooth, and appearing as a single mass. Lead scans on the fines (Figure 25B) revealed an even or uniform lead concentration. These differences observed are at the limit of the capabilities of the x-ray detection system and may not be highly accurate. Fines as shown in Figure 25A and 25C did show lead concentrations to be greater than the background fines. Since the fine particles do indicate the presence of lead, the indication of lead in all particles is evidently due to the Andersen Sampler collection system.

4) X-ray Spectra of Impingement Areas - The non-dispersive x-ray spectrometer is quantitative only when running standards with samples. However, relative ratios can be determined when comparing various samples run under identical conditions. Such is the case with the attached graphs. Relative intensities were compared and plotted as Pb:Cl:Br on trays 1, 3, and 6 for runs #8 through #14 (Figures 26-31). Relative ratios appear very similar on the final filter when both Cl and Br are present. Likewise the Pb:Cl:Br is nearly identical on plate 6 and the filter. Plate 1 shows a higher Cl:Br ratio with plate 3 reversing that ratio, and plate 6 being $\sim$1:1. These trends are followed in runs #11 through #14.

f. Discussion

The SEM with non-dispersive x-ray can readily distingusih between diluent air blank, lead, lead + EDB, and lead + EDC runs. Information is too uncertain on the non-leaded (#5) run to be sure of that identification. Individual particles are characterized and future work with SEM + x-ray fluorescence + x-ray diffraction will yield positive identification on crystal type and formula. The particle $<10\mu$

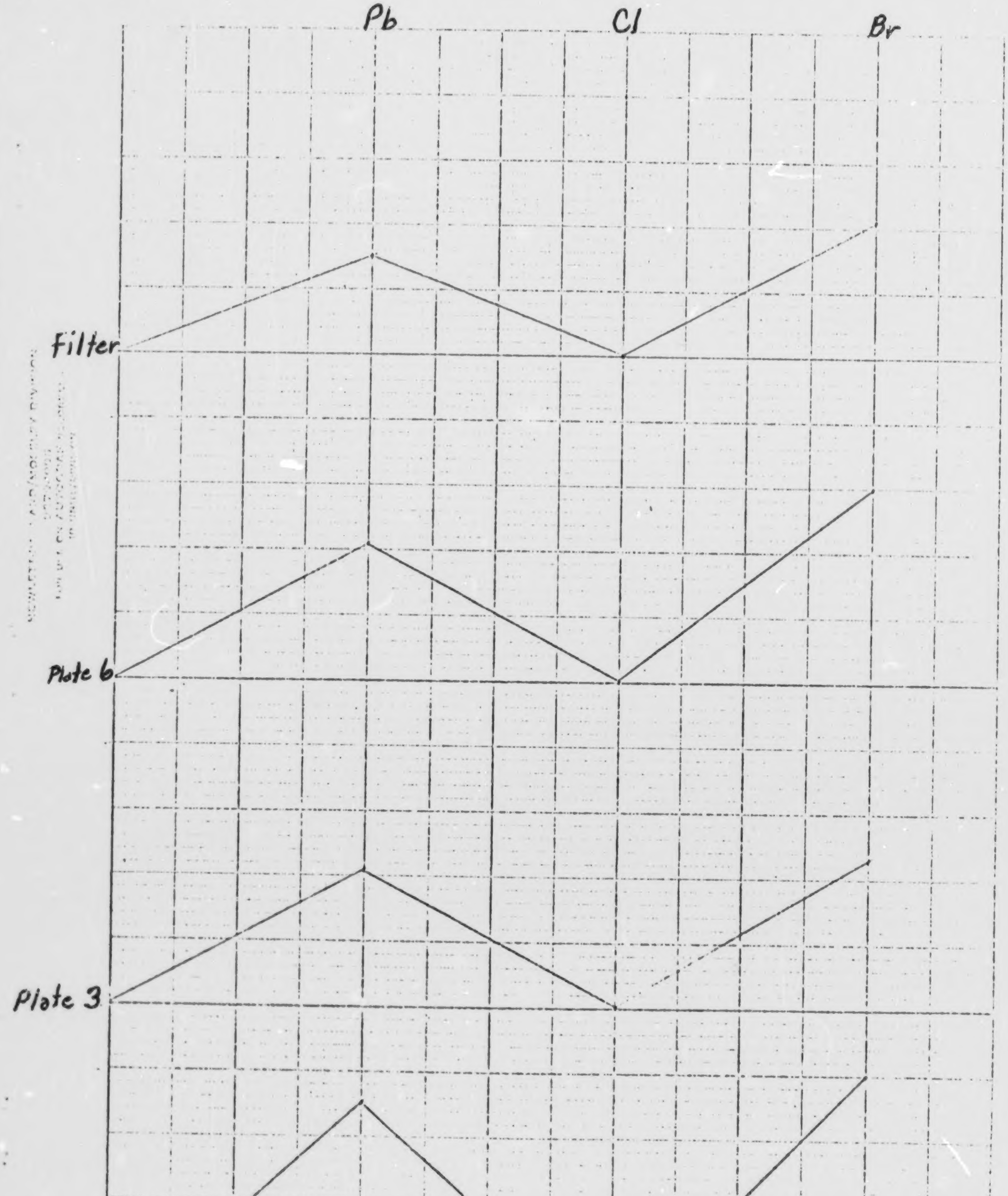
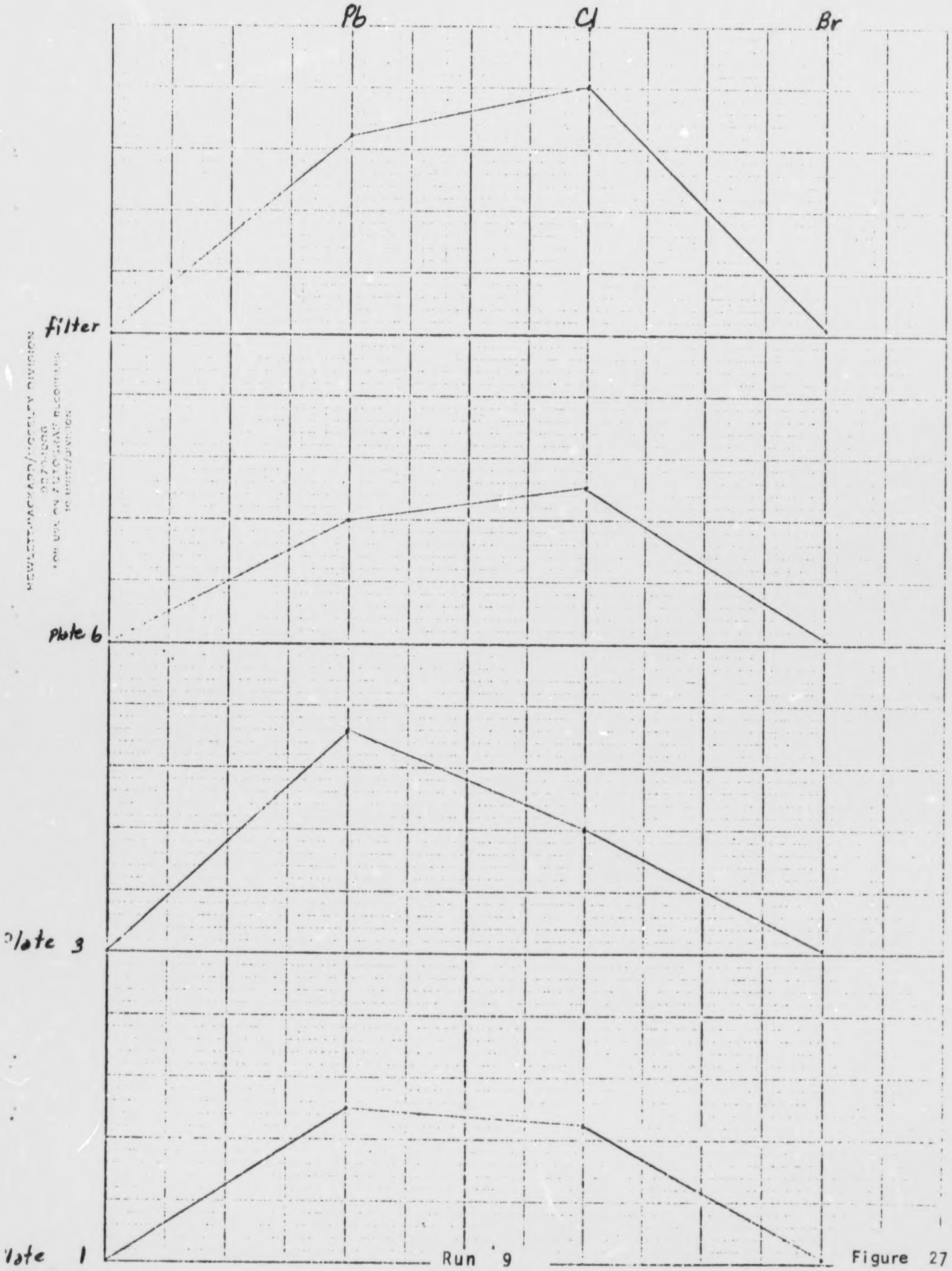


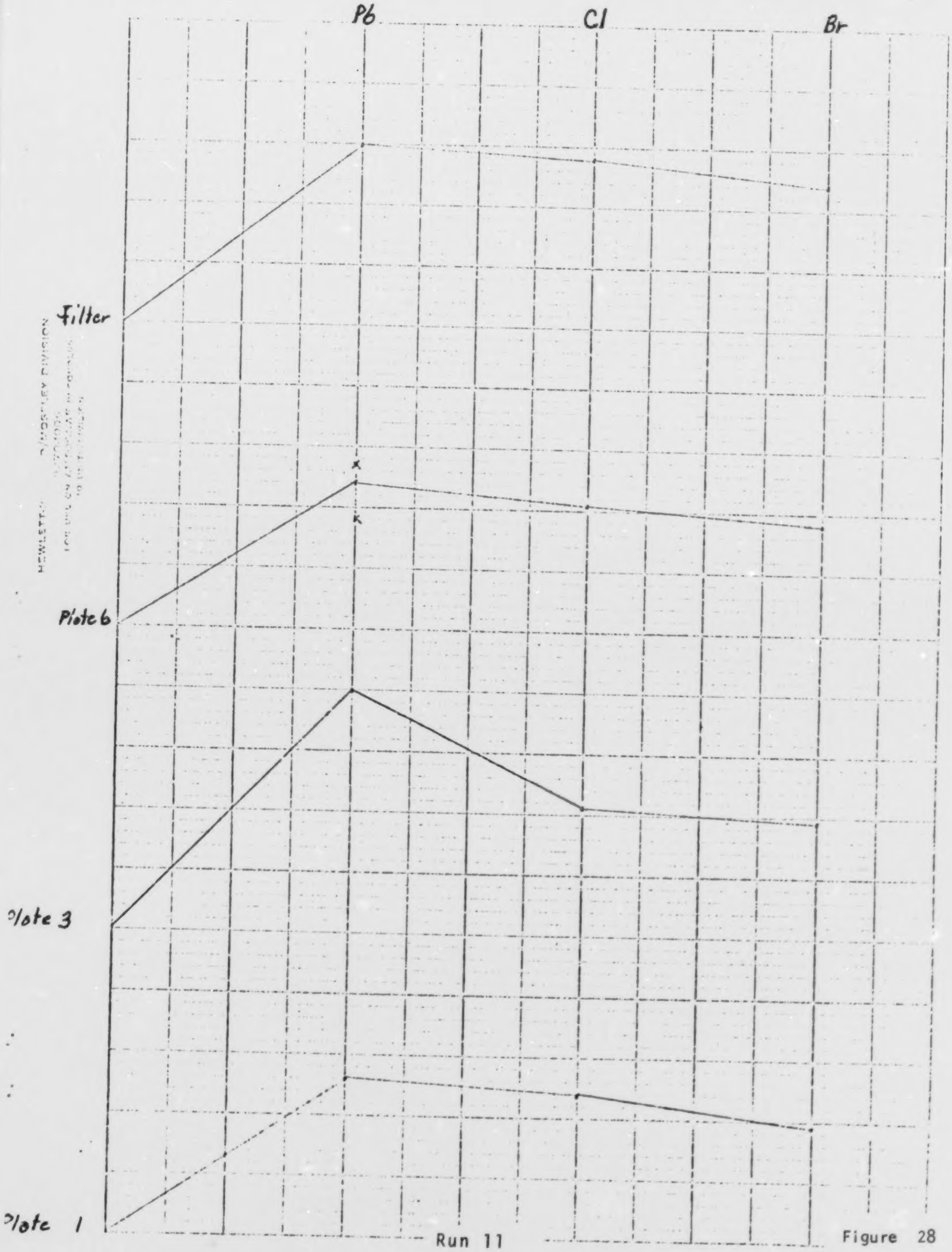
Figure 26

Run 8



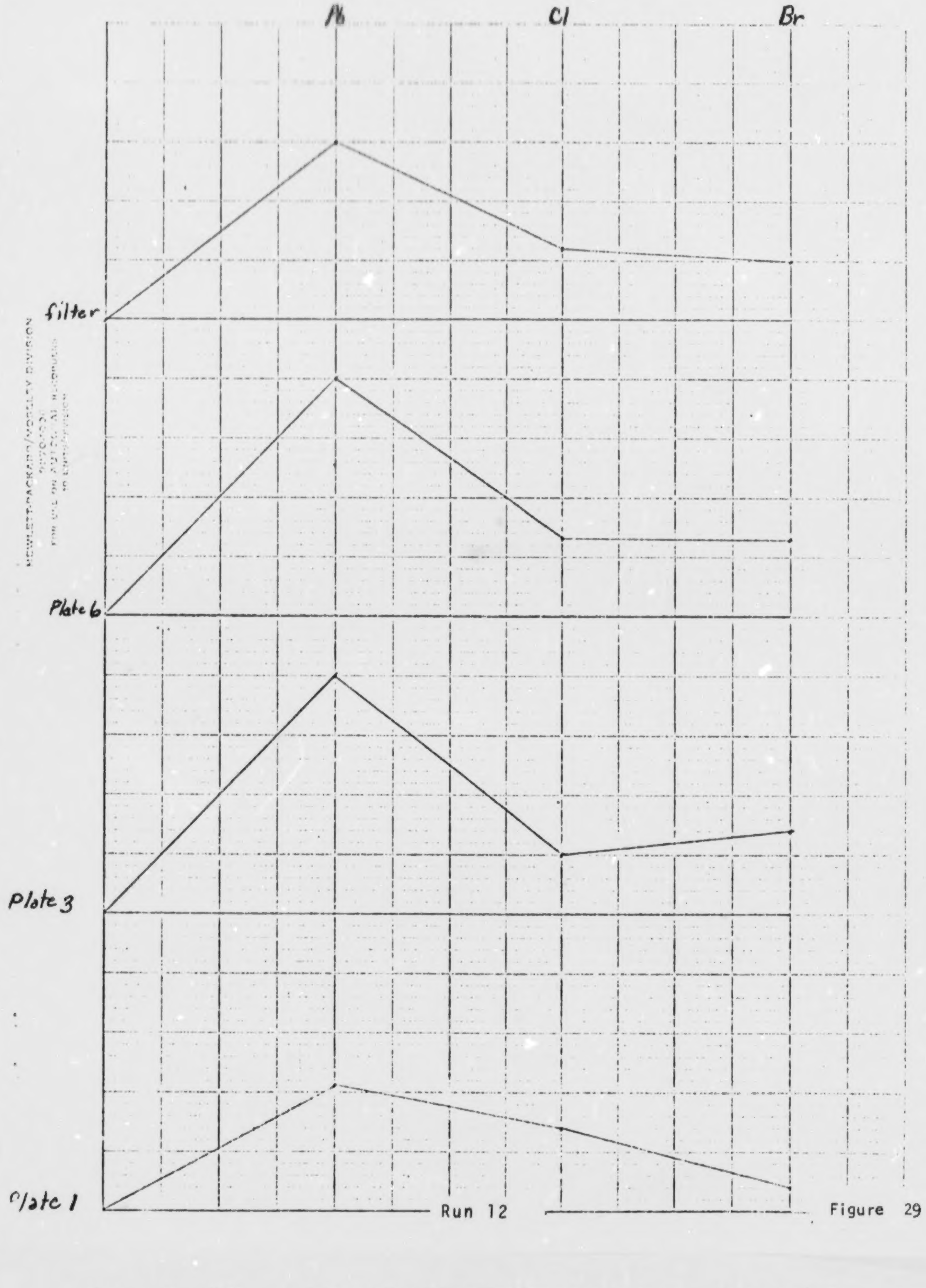
Run 9

Figure 27



Run 11

Figure 28



Run 12

Figure 29

HEWLETT-PACKARD/MOSELEY DIVISION

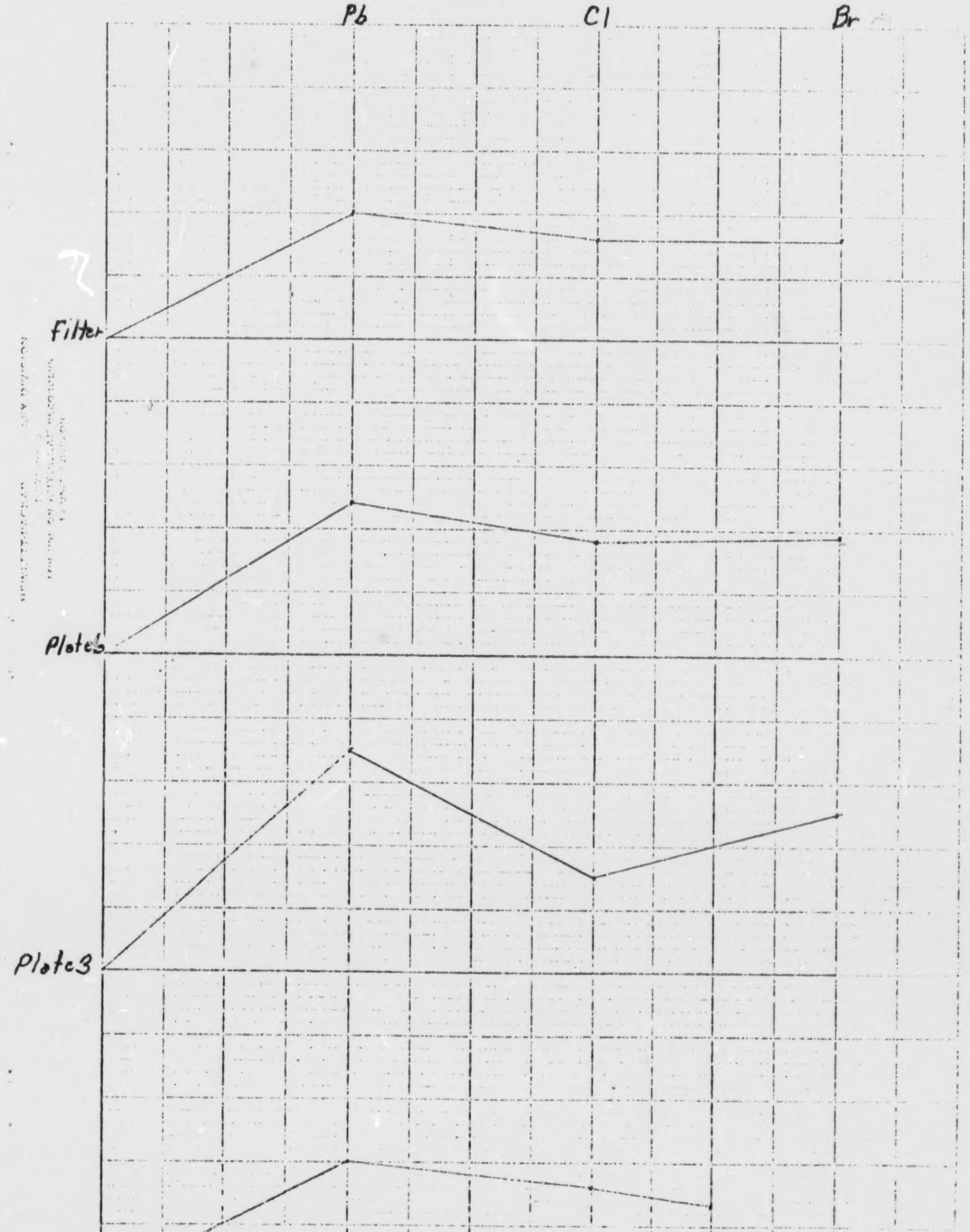


Figure 30

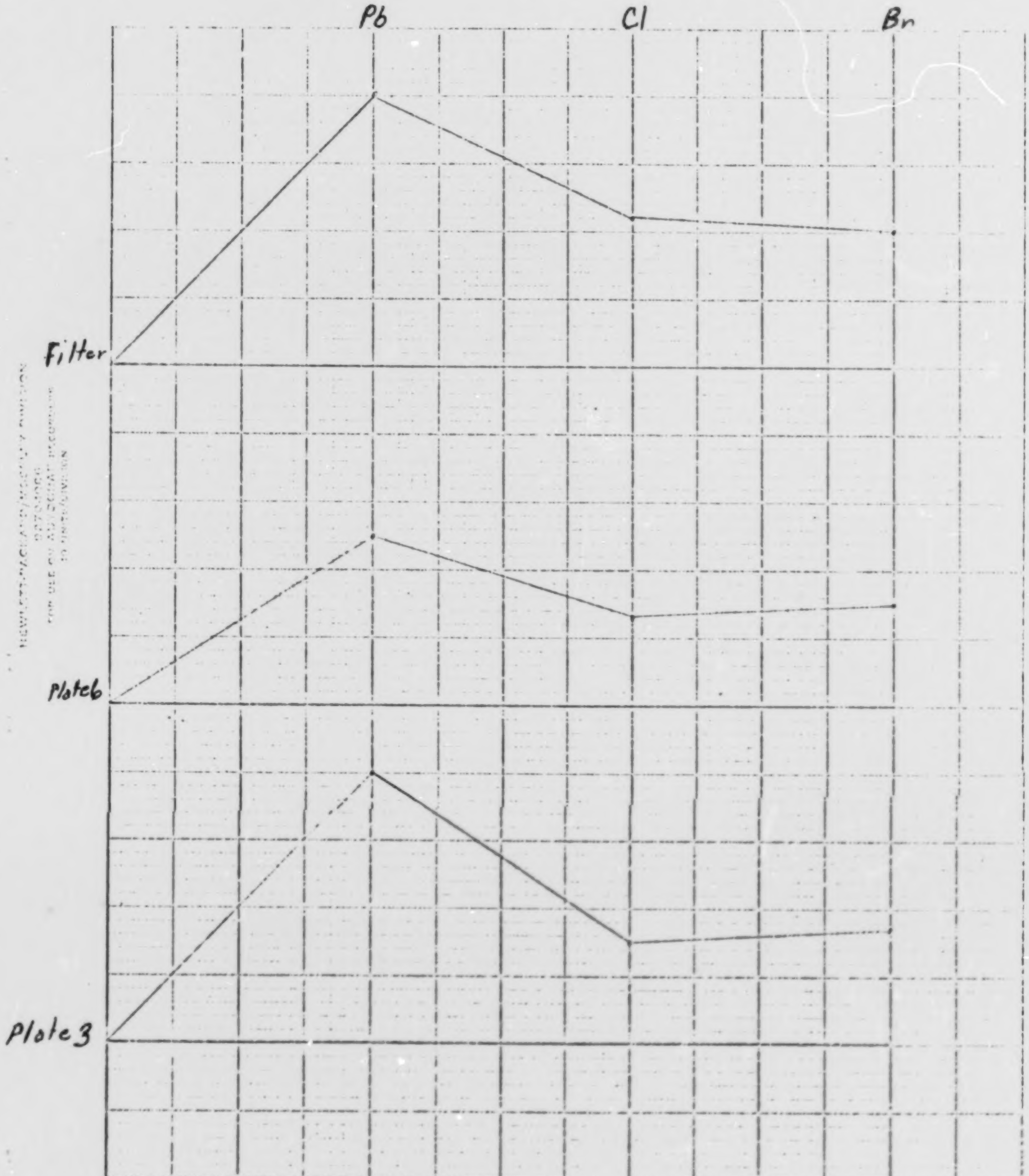


Figure 31

can also be identified using SEM for characterization and electron diffraction for identification with mapping of finder grids. Thus far the qualitative approach to individual particles has been used. In the future a frequency distribution will make the results more quantitative as well as qualitative.

Scanning Electron Microscope Photomicrographs and X-Ray spectrum for several runs are shown in figures as noted below:

Table 16

SCANNING ELECTRON MICROSCOPE PHOTOMICROGRAPHS
AND X-RAY SPECTRUM FIGURE DESIGNATIONS AND
DESCRIPTIONS

Run #7	Indolene HO 0 + 3 ml/gal TEL
Figure 32	5000X Plate #1 Andersen Sampler
Figure 33	10,000X Plate #1 Andersen Sampler
Figure 34	20,000X Plate #1 Andersen Sampler
Figure 35	Various X Plate #6 Andersen Sampler
Run #8	Indolene HO 0 + 3 cc/gal TEL + 1t EDB
Figure 36	10,000X Plate #3 Andersen Sampler
Figure 37	20,000X Plate #3 Andersen Sampler
Run #9	Indolene HO 0 + 3 cc/gal TEL + 1t EDC
Figure 38	Various X Plate #1 Andersen Sampler
Figure 39	10,000X Plate #1 Andersen Sampler
Figure 40	20,000X Plate #1 Andersen Sampler

Figure 32

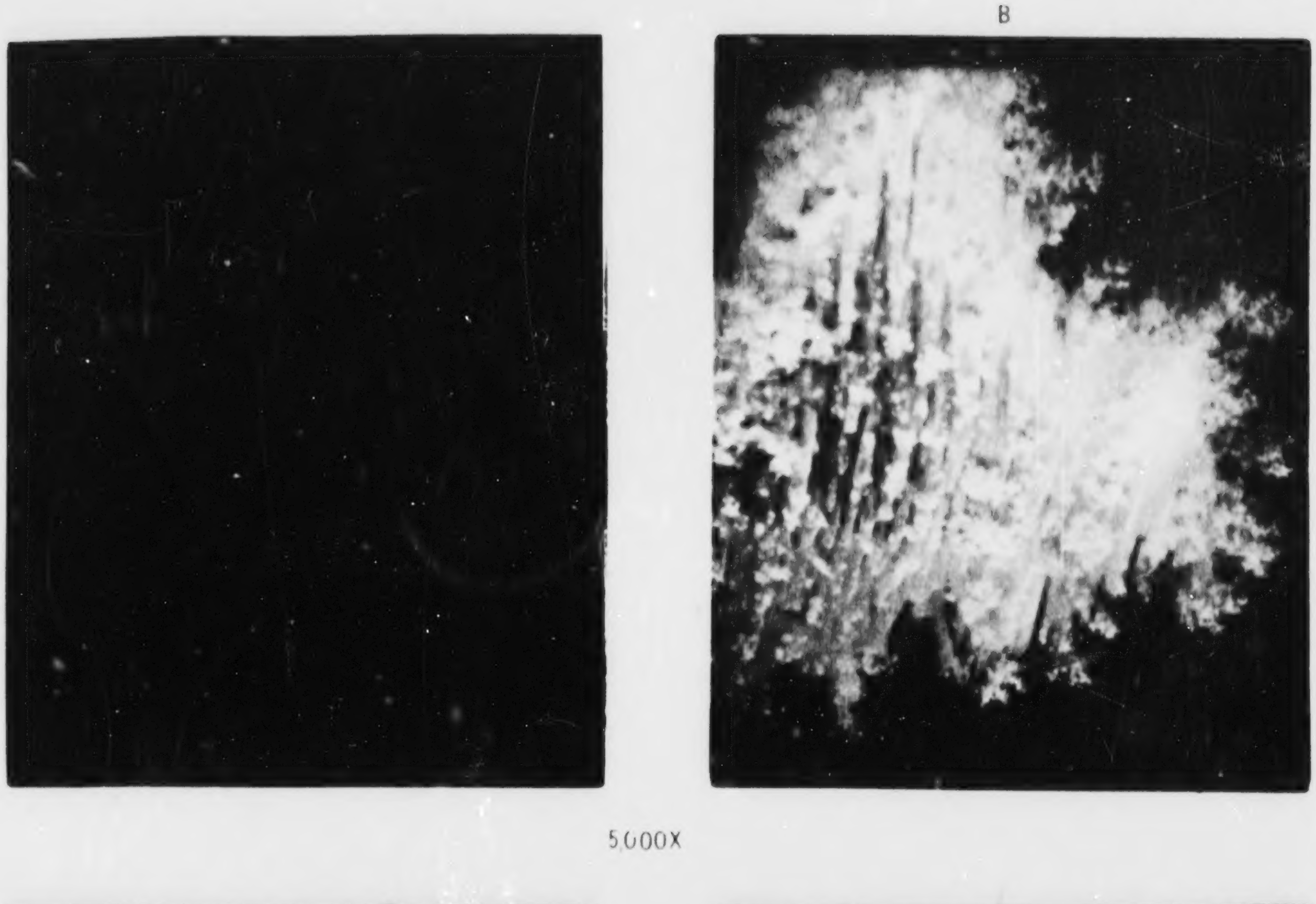


Figure 33

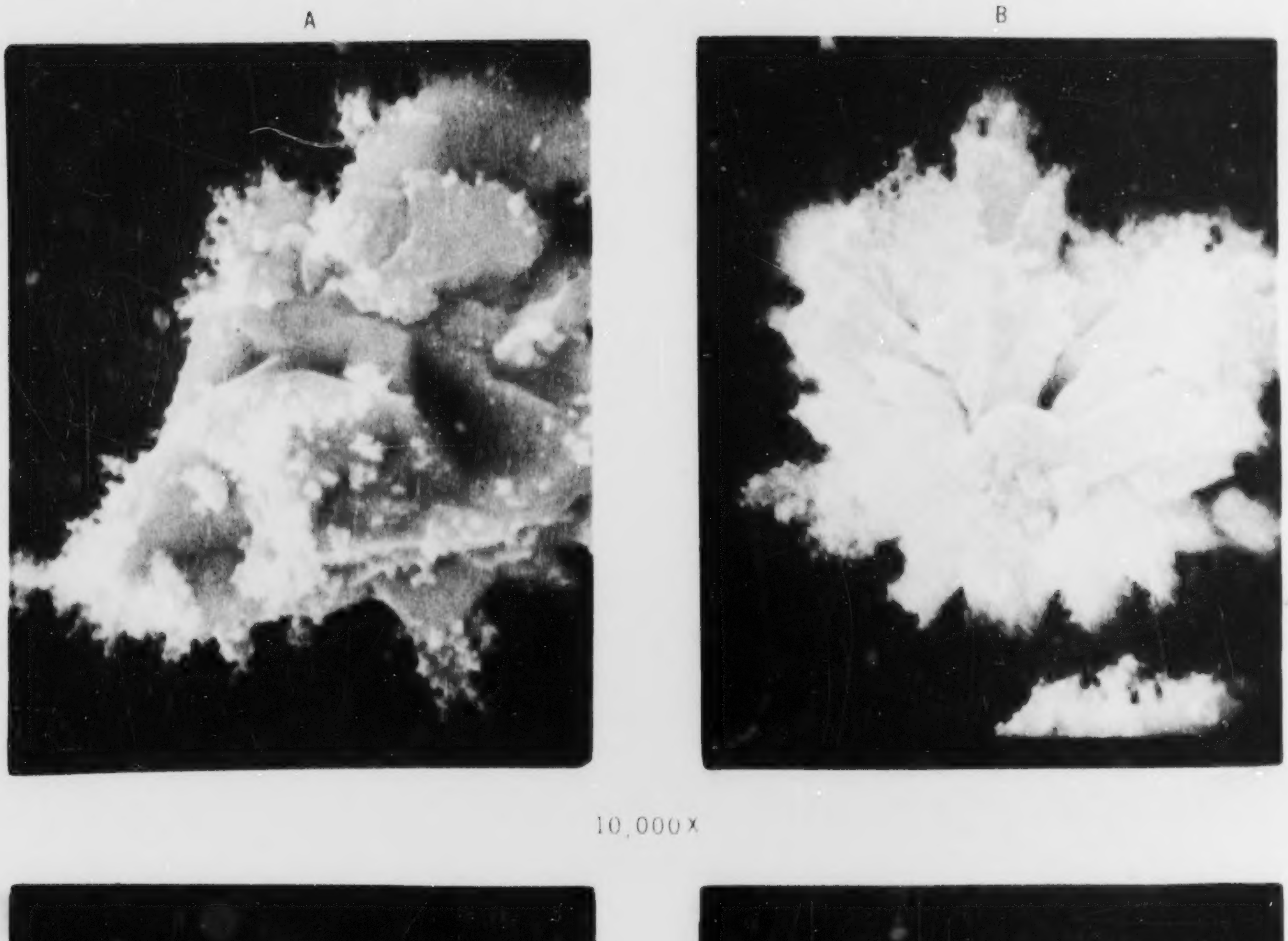

A
B
10,000X
C
D

Figure 34

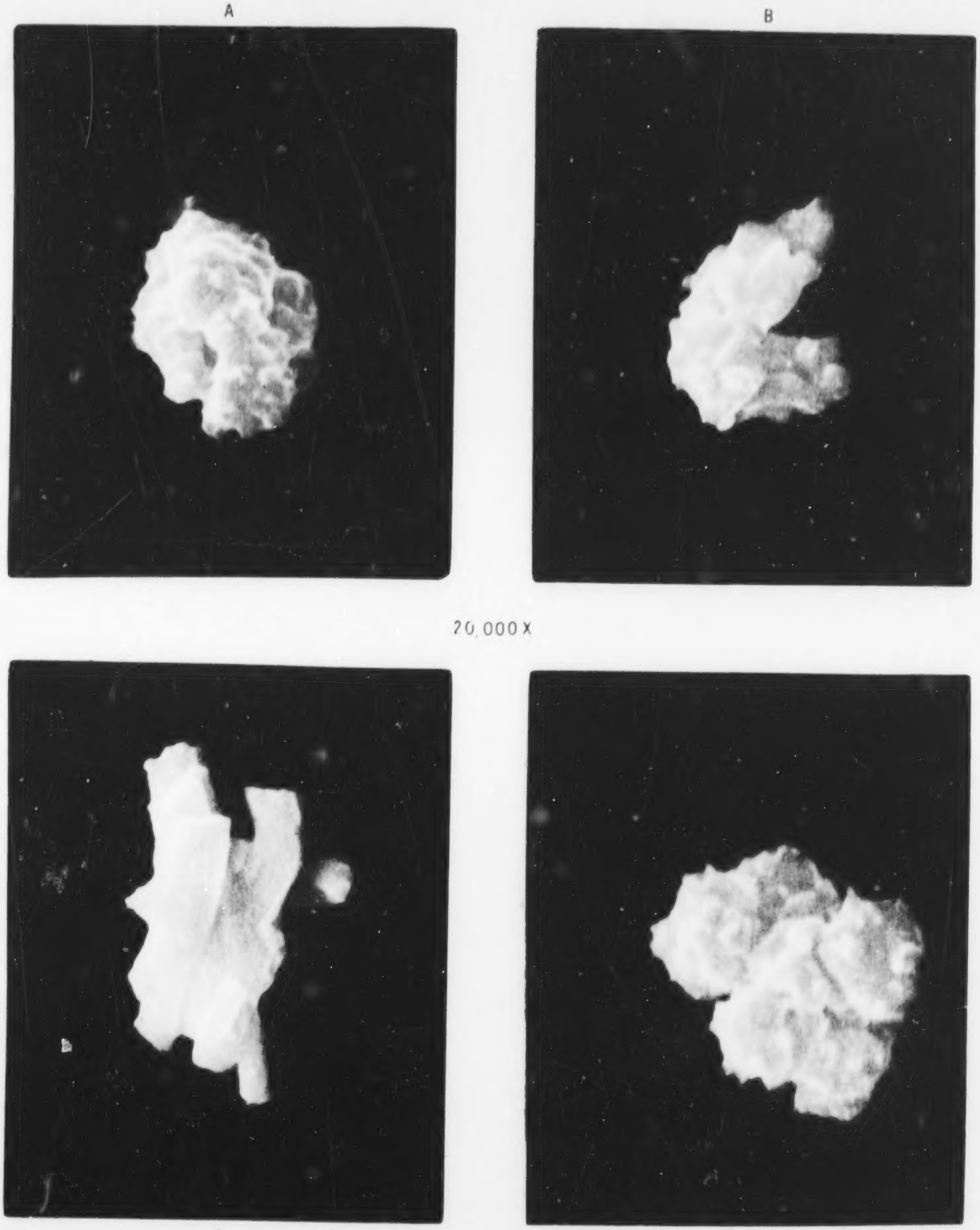
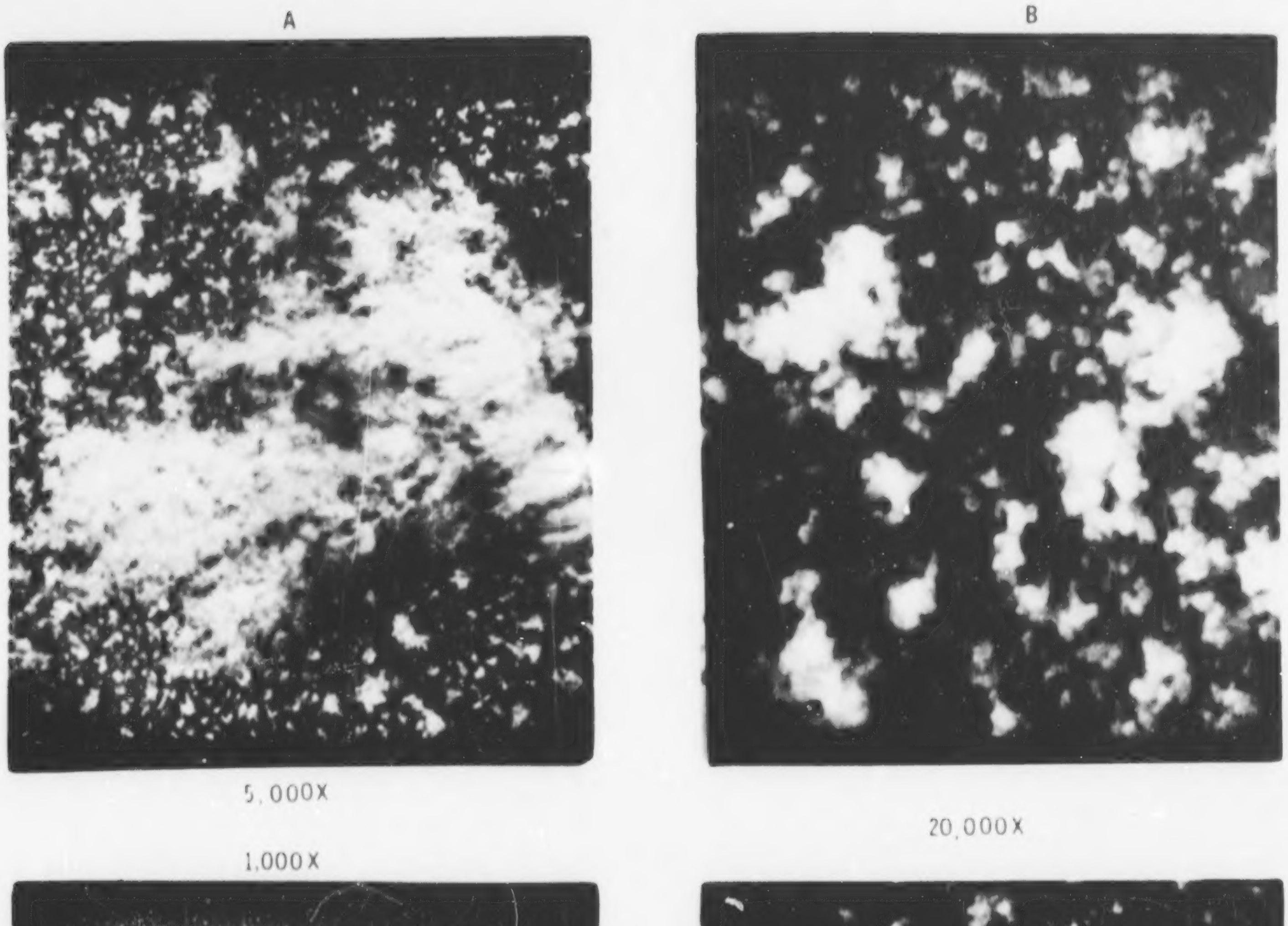

A
B
20,000X
C
D

Figure 35



A 5,000X

B 20,000X

C 1,000X

D

Figure 36

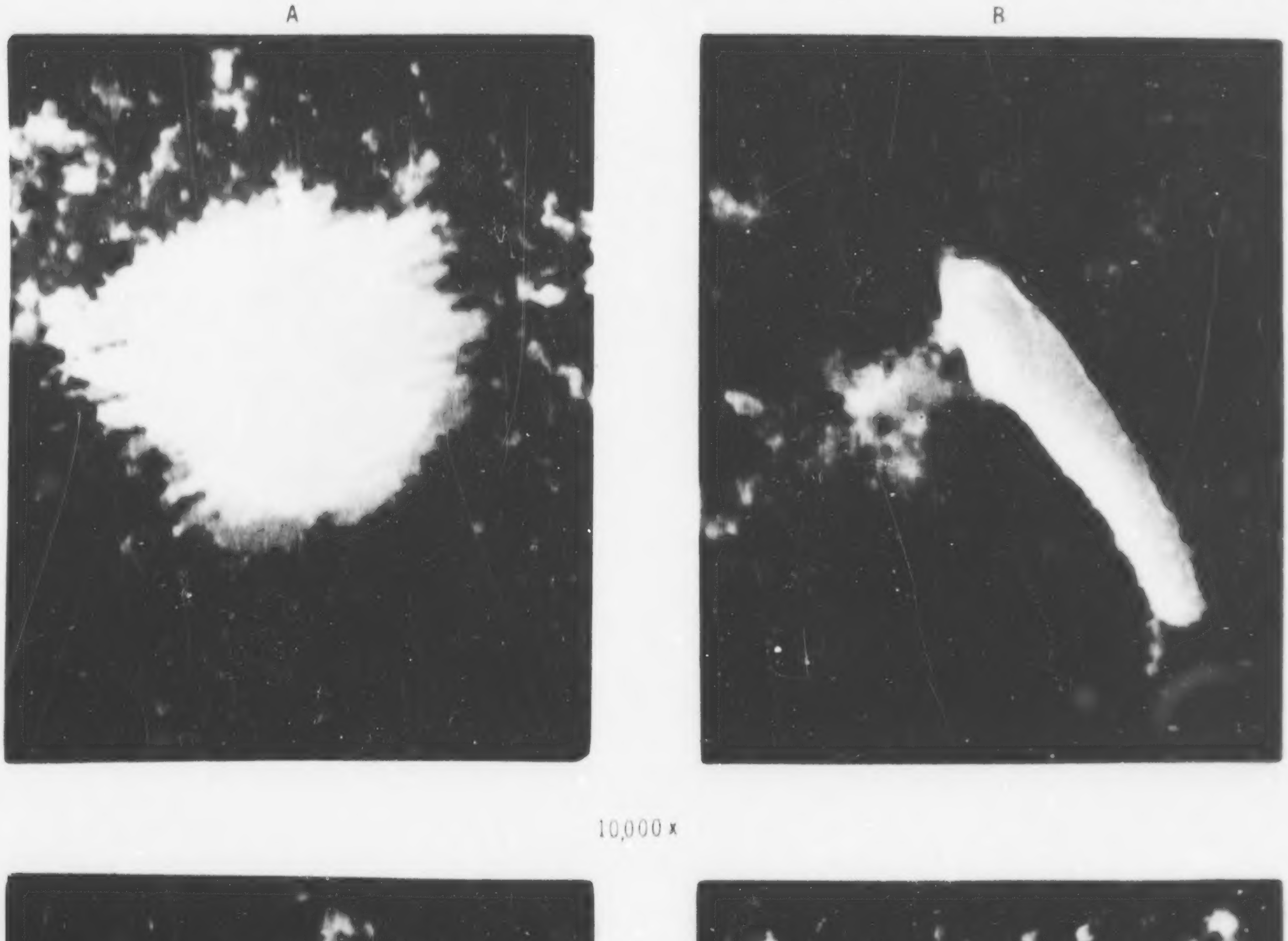

A
B
10,000 x
C
D

Figure 37

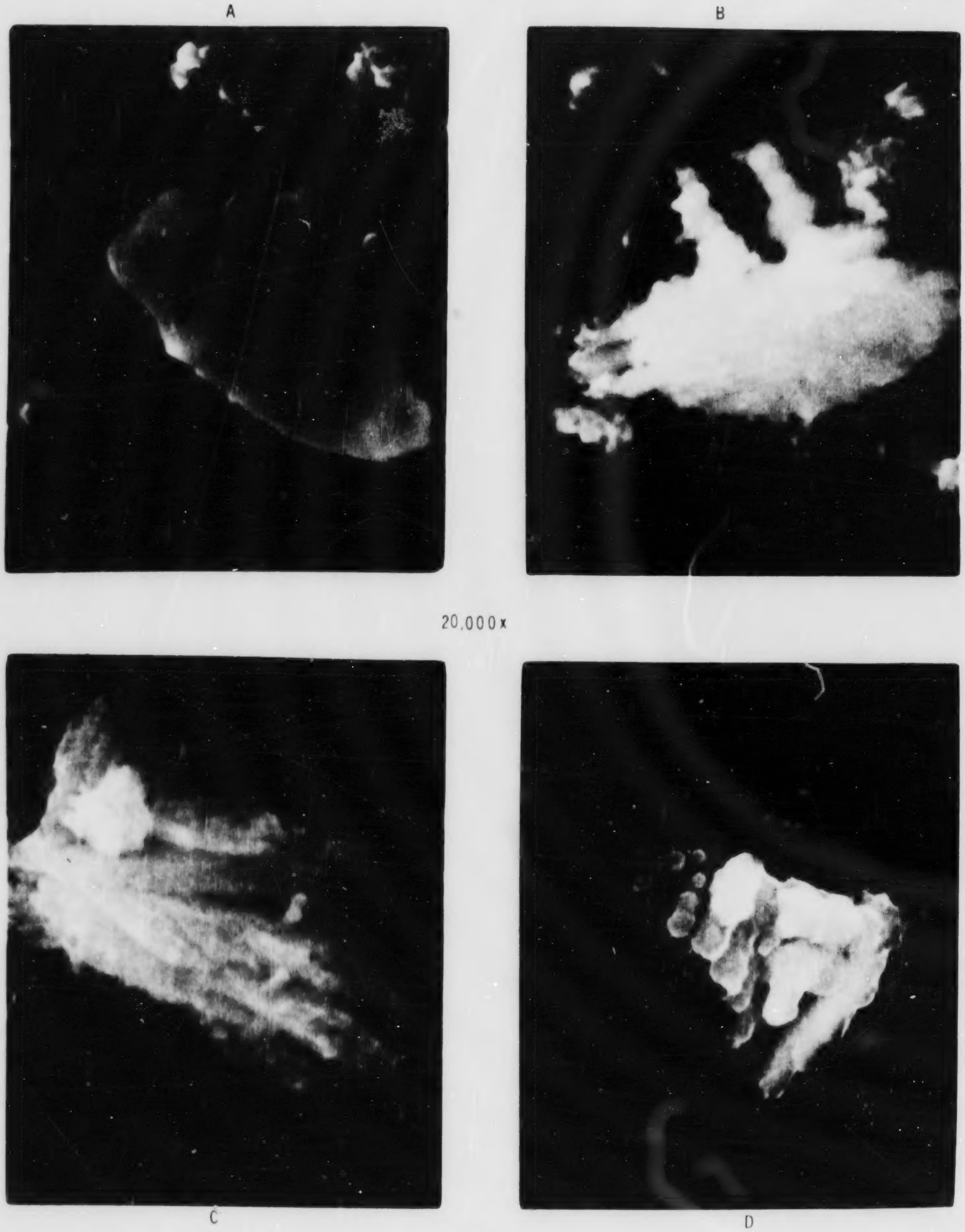
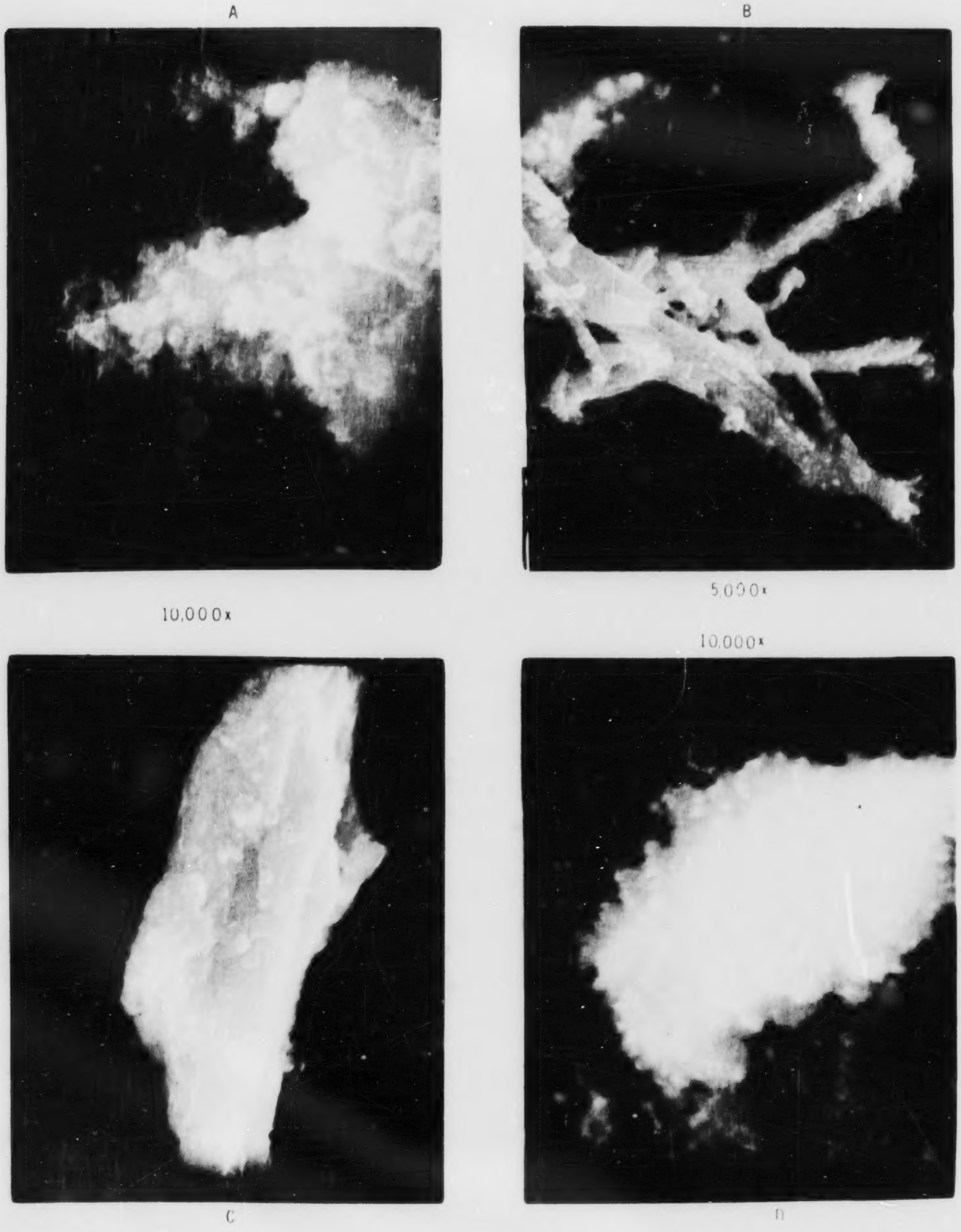

A
B
20,000x
C
D

Figure 33



A

B

10,000x

5,000x

10,000x

C

D

Figure 39

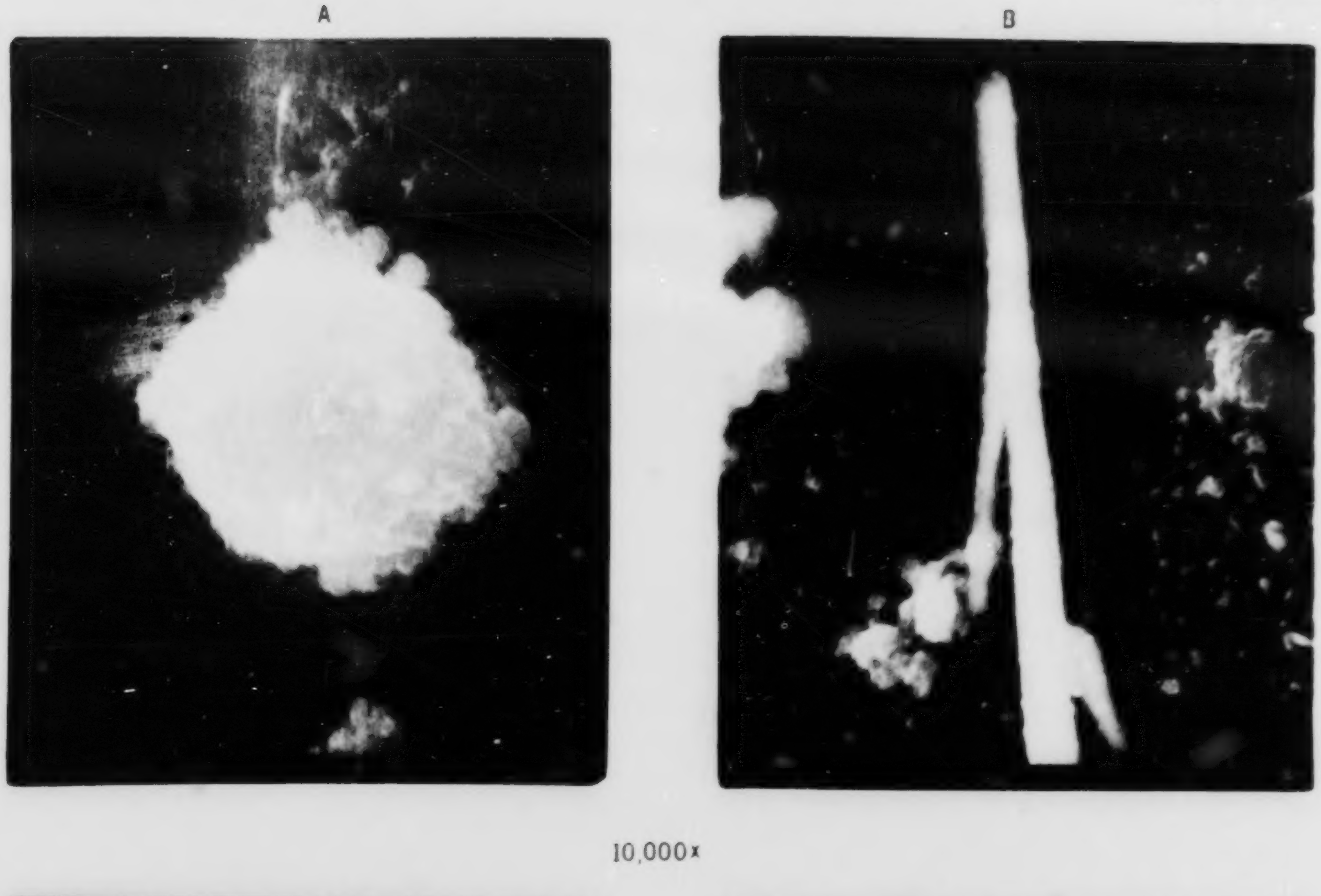
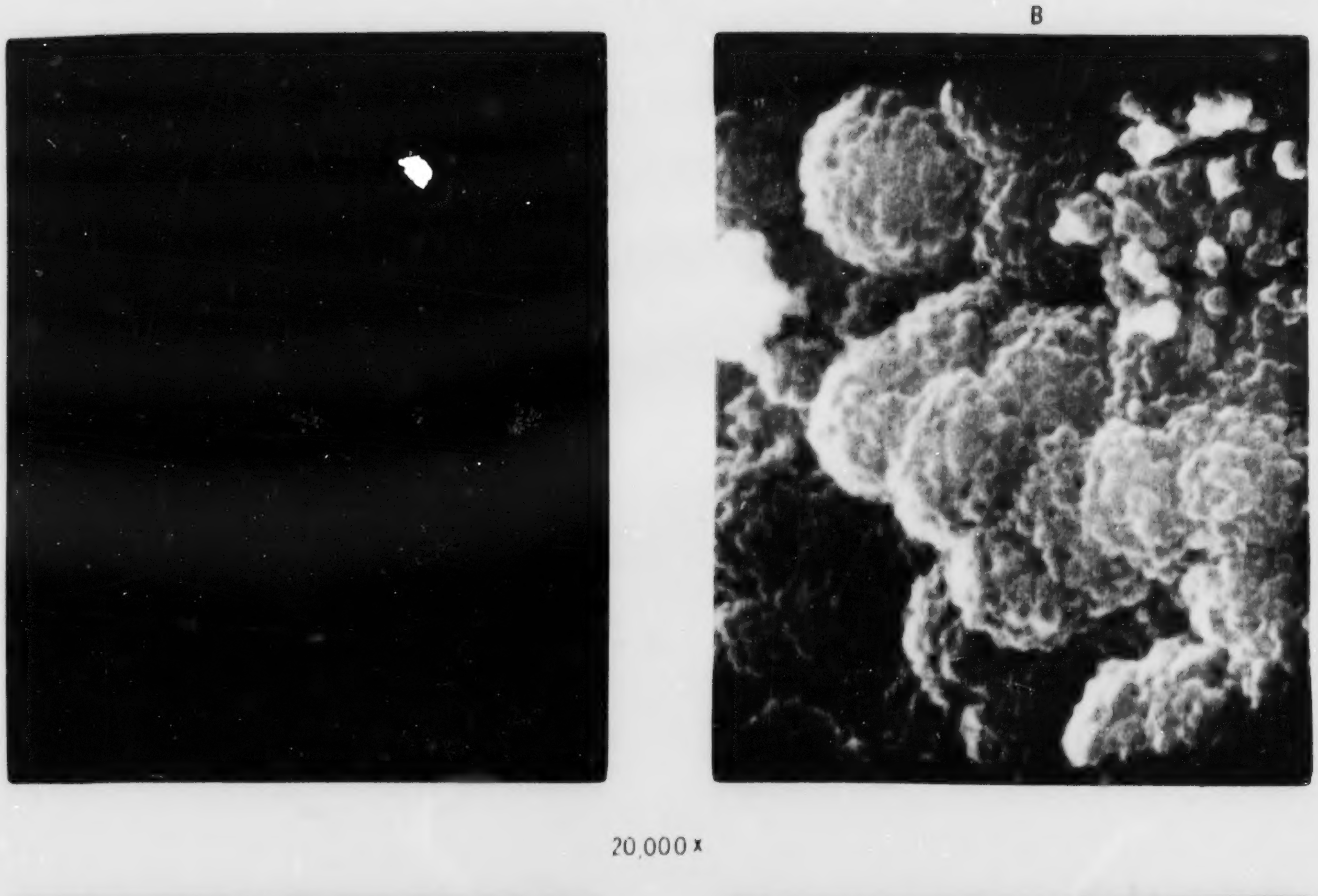

A
B
10,000x
C
D

Figure 40



Run #11	Indolene HO 30, Steady-State Sampling
Figure 41	1000X and 2000X Left side, particles plate #1 Andersen Sampler Right side, Pb scan of same areas with x-ray detector
Figure 42	5000X (B) Plate #1 Andersen Sampler (C) Pb scan (B) area (D) Cl scan (B) area
Figure 43	10,000X and 20,000X Plate #6 Andersen Sampler
Figure 44	X-Ray Spectra (D) Particle Figure 55

3. Light Microscopy and X-Ray Characterization - (Howard Garrett, S. Rinn)

a. Purpose

This part of the microscopy analysis can be divided into two sections: (1) Documentation at low magnification to show the particle distribution and several impingement points on collection plates 1, 3, and 6 of the Andersen Sampler. (2) Documentation of particle size range and character using polarized light at 400X on plates 1, 3, and 6 of the Andersen Sampler, plus the Millipore filter. X-ray diffraction identifications were made on these same samples by H. W. Rinn of the Chemical Physics Research Laboratory. An effort was made to correlate crystal character (as seen by polarized light) with chemical and physical composition.

b. Results

The main purpose of the low magnification photomicrography was documentation. There were differences between runs and this work can be considered as a reference point in judging

Figure 41

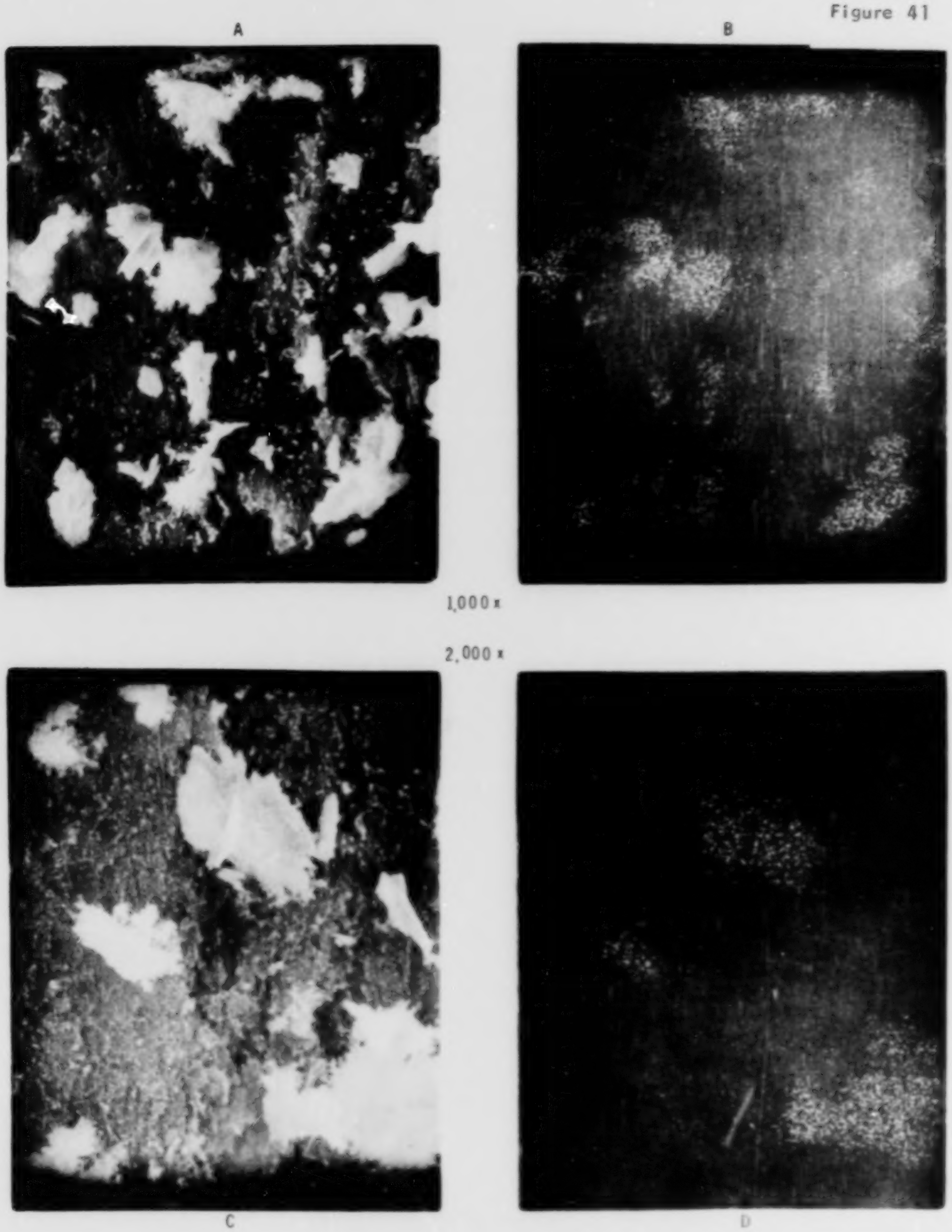

A
B
1,000 x
2,000 x
C
D

Figure 42

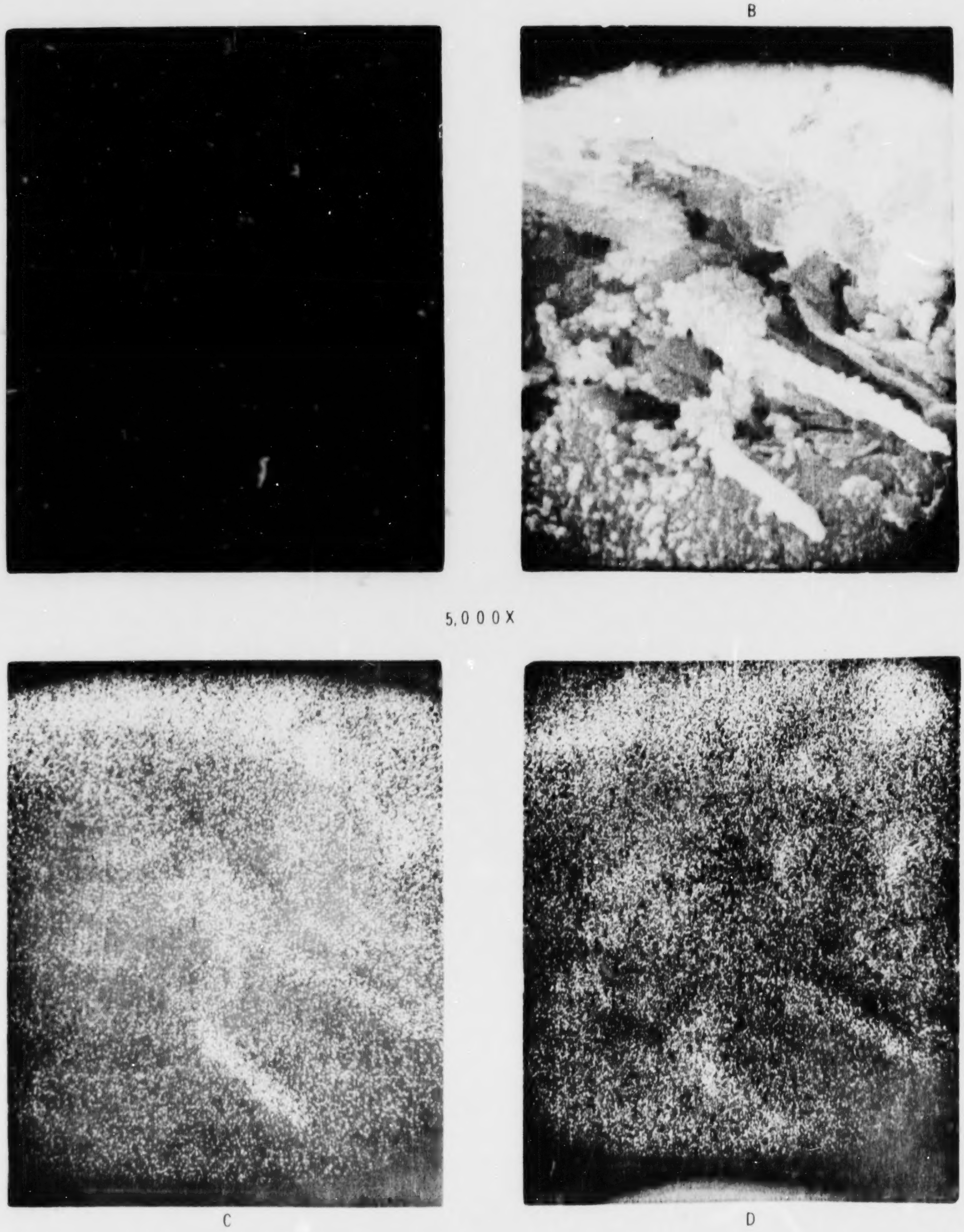


Figure 43

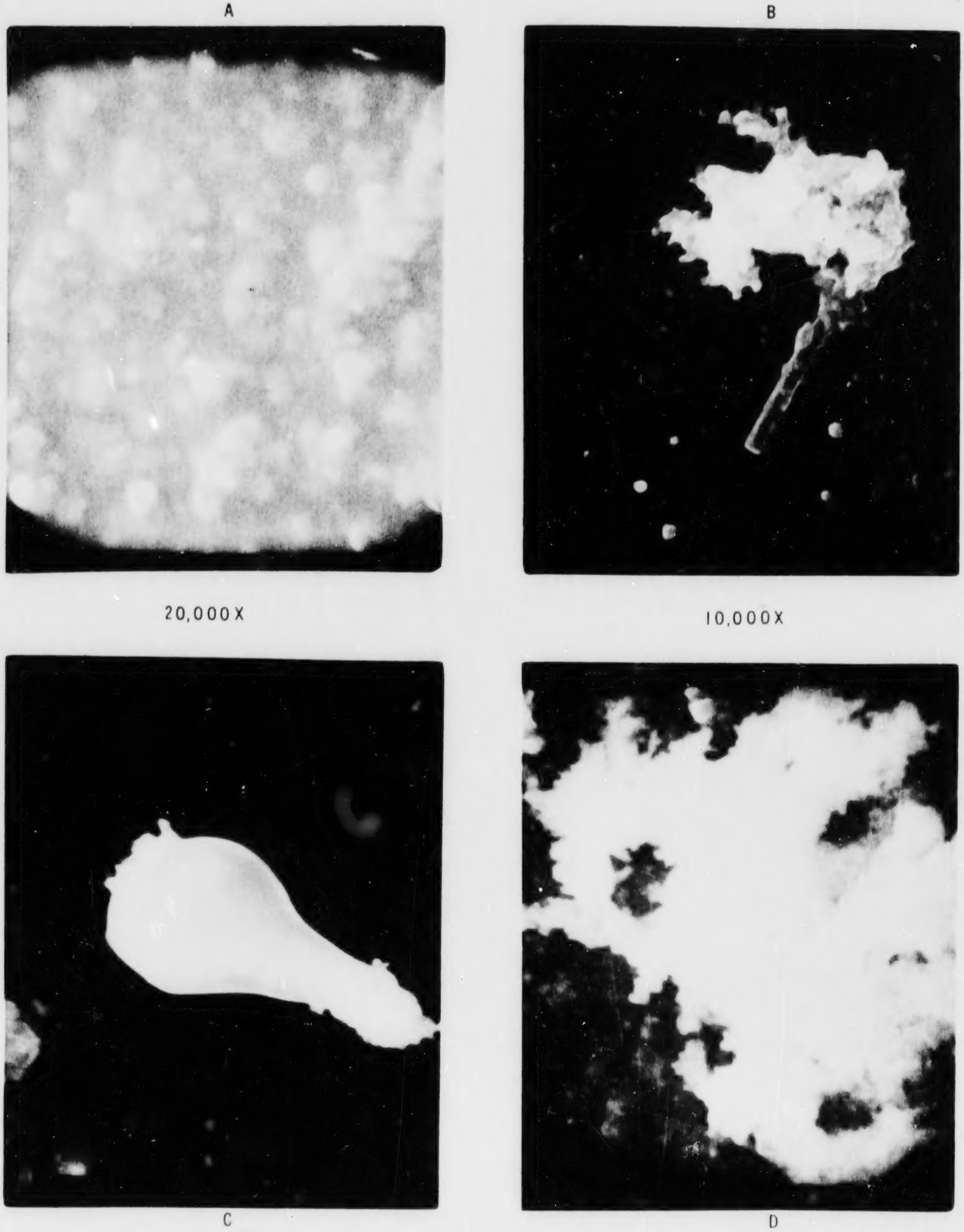
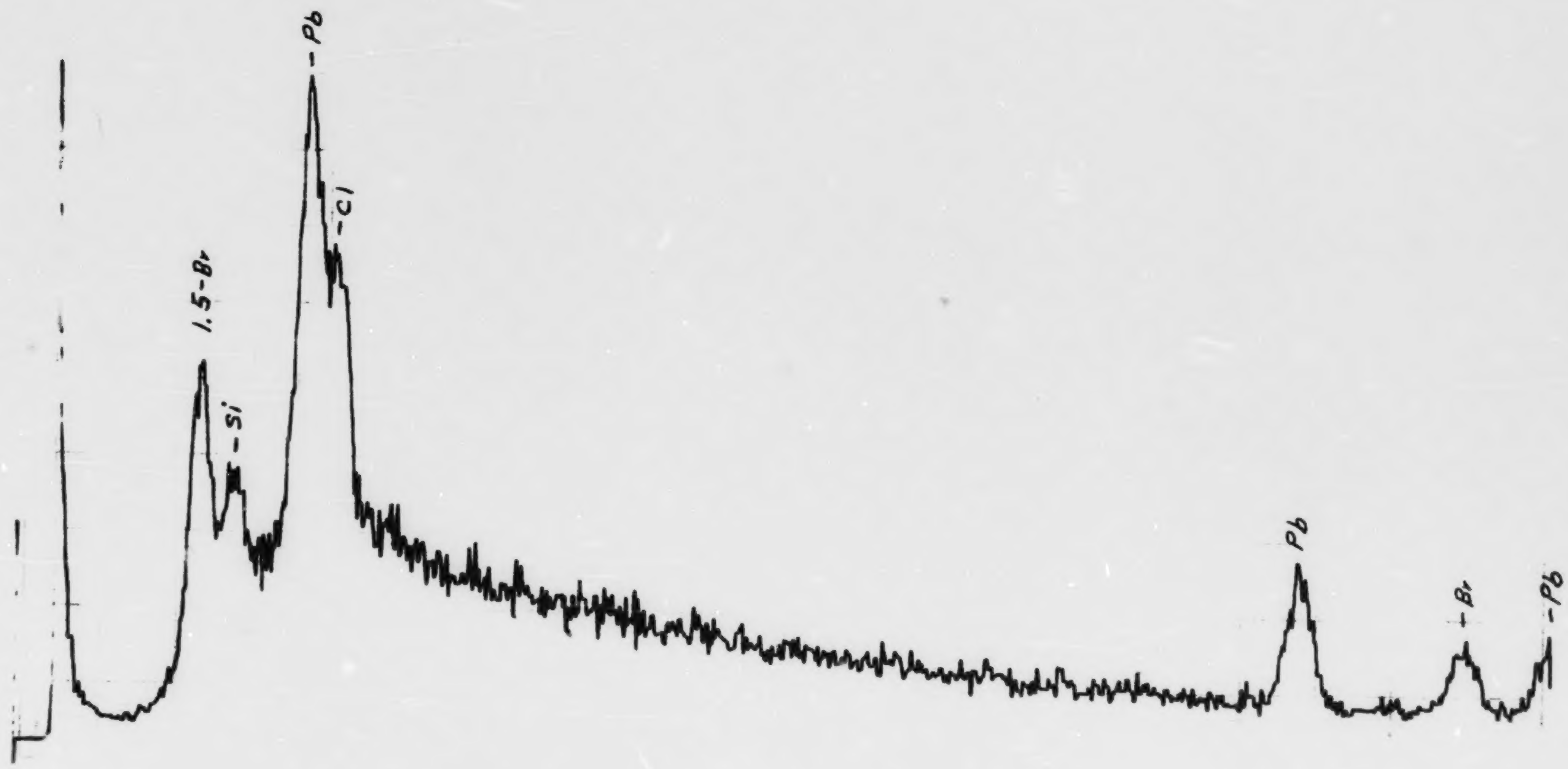

A
B
20,000X
10,000X
C
D

Figure 44



or describing some aspects of the higher magnification work. This work also shows a rough comparison of the amount of material on a particular plate of different runs and compares an actual run with a diluent air blank run.

The polarized light microscopy and the attempt to correlate the polarized light microscopy with x-ray diffraction identifications have not been as informative as was hoped for, but nevertheless have produced some valuable information. The x-ray diffraction identification of the crystalline species has been invaluable as this technique has been able to identify the different crystalline species from the various runs and has even shown different species on the various trays of the Andersen Sampler and Millipore filter of a given run.

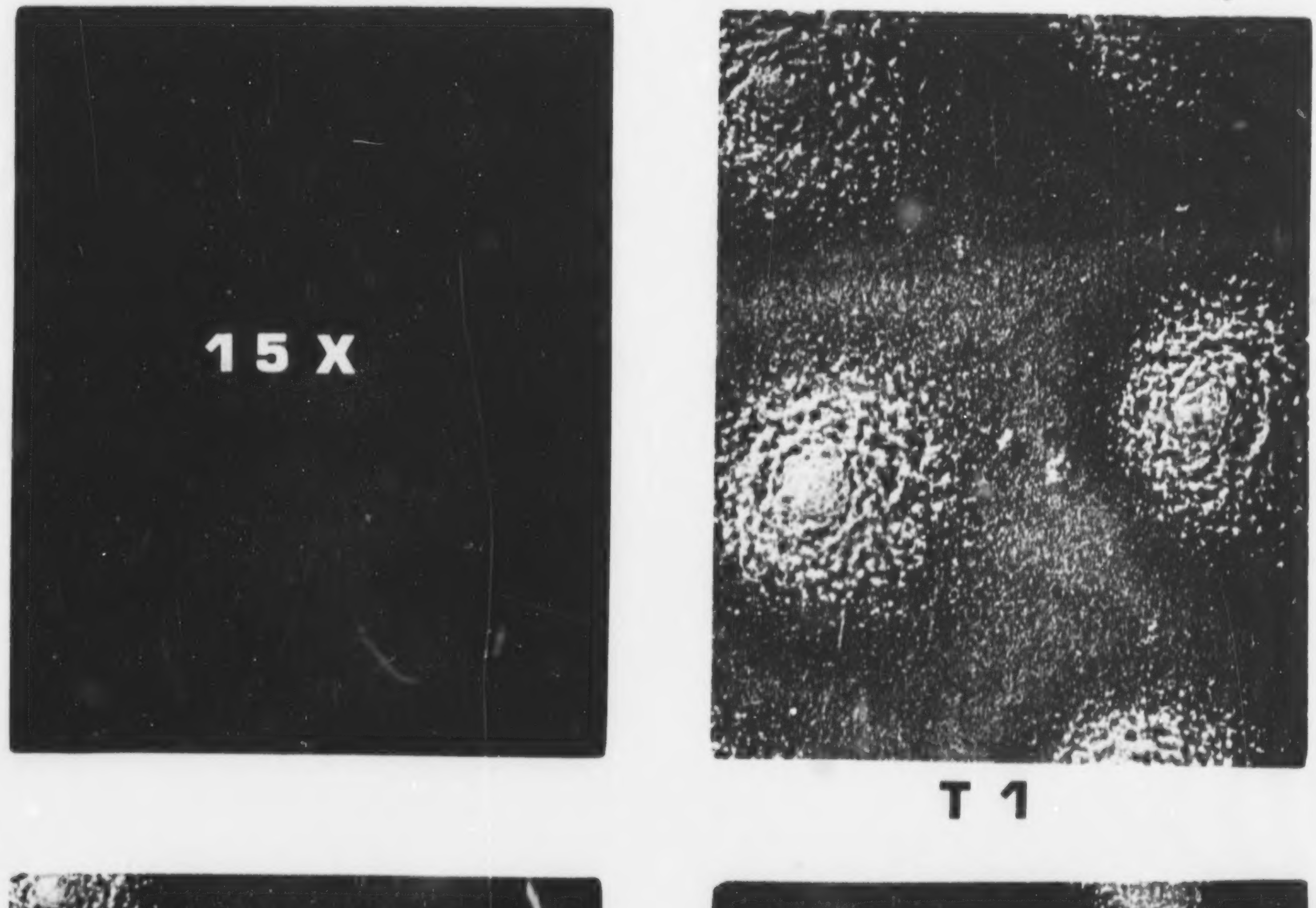
Judging from the photomicrographs (15X) there is a vast difference in the quantity of material collected on a sample run (Figure 45) as compared to a blank run (Figure 46). There is considerable variation in the amount of material and the pattern of the deposit within the various sample runs. The remainder of the results will be divided into several topics.

c. Particle Size

Although gross variations occur between some runs, we can make some broad generalizations as follows:

1. The particles on plate 1 are usually in the 5-20μ range.
2. The particles on succeeding plates gradually decrease in size until plate 6 has most of its particles in the 1μ range although larger particles may be found also.
3. The Millipore filter has the finest particles (1μ and below) although Run #8 had clear particles as large as 30μ on this filter.

Figure 45

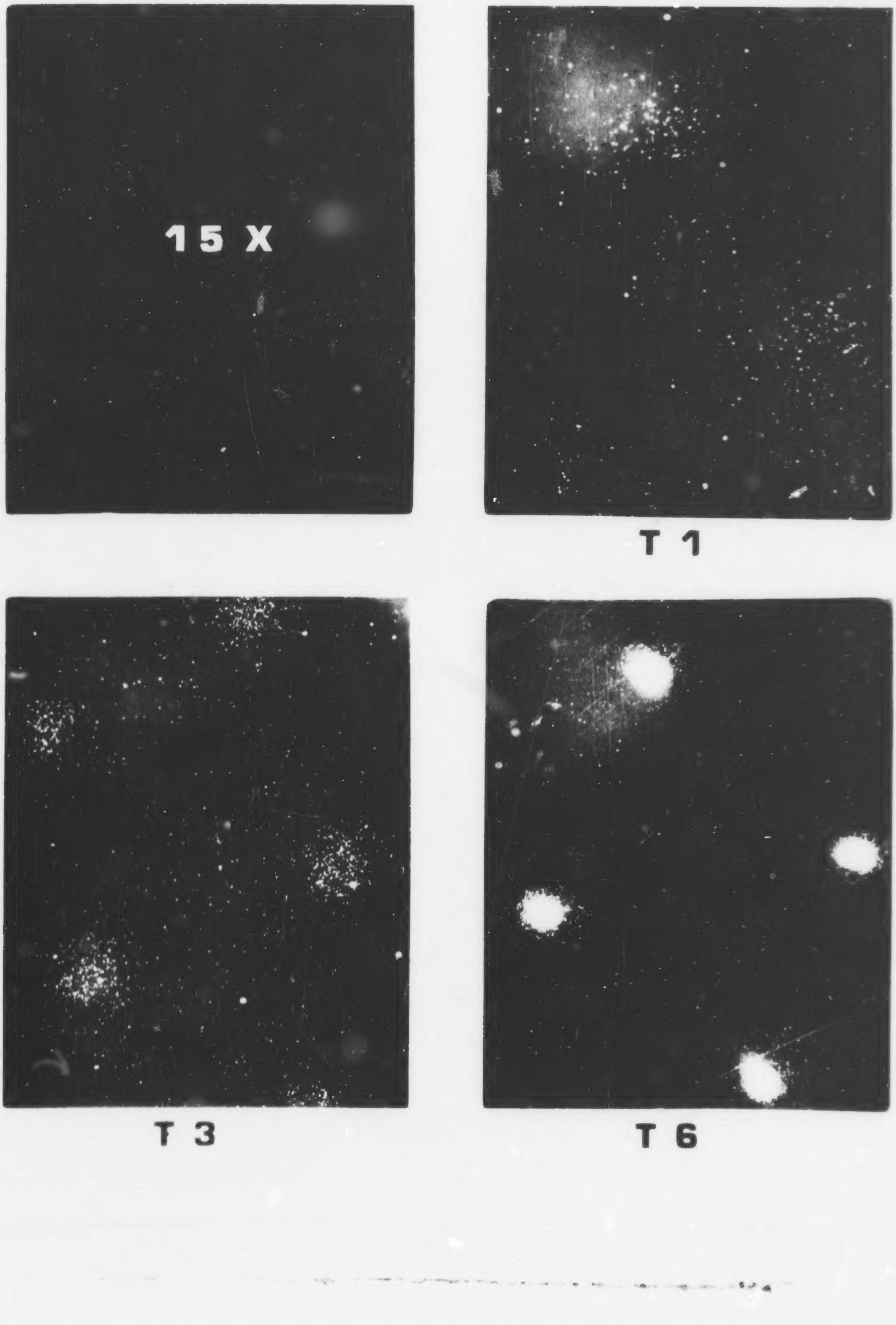


T 1

T 3

T 6

Figure 46



T 1

T 3

T 6

d. Particle Description

1) Diluent Air Blank Run - This consists of a wide variety of particles which might be classified as dirt and contains such species as (a) spherical, glassy fly ash particles and (b) highly birefingent particles which are probably calcite. Calcite may be used in scouring powders and could originate from that source. Traces of calcite are observed in most runs, especially on plate 3. Such trace quantities are not detected by x-ray diffraction.

   On blank runs 6-B and 7-B lead compounds from the engine which was being cycle conditioned in the test cell were also detected - especially on plate 3.

2) Sample Runs - The major particles varied from single transparent crystals to translucent agglomerates. The external morphology of the particles is impossible to define by polarized light microscopy but this is described under SEM and x-ray. Although several crystalline species have been identified by x-ray diffraction, it has not been possible to identify these particles by polarized light alone because of the similar morphology of the different crystalline species. Also a particular species such as lead chlorobromide may appear as transparent single crystals in one run (#11) and appear as translucent agglomerates in the next (#12).

   Black opaque particles are usually present on plates 1 and 3 and they are probably flakes of Fe_3O_4 from the wall of the exhaust system.

e. Color

The preliminary samples which were received when the methods were being developed showed some color variations so color film was used. However, later samples have not shown significant color worth recording so the use of color was discontinued after Run #4.

f. Chemical Composition and Crystal Species

This portion of the report is the work of H. W. Rinn of the Chemical Physics Research Lab. Although some variations do occur, we can make the following general conclusions:

1. The most common solid particulate from Indolene HO 30 gasoline is lead chlorobromide with an unknown species designated as UP 1875 also present. The UP 1875 appears to be another crystallographic form of lead chlorobromide.

2. Leaded gasoline in combination with ethylene dibromide gives lead bromide plus a bromine rich form of UP 1875.

3. Leaded gasoline in combination with ethylene dichloride gives lead chloride plus a chlorine rich form of UP 1875.

4. Leaded gasoline without scavengers produced chiefly $4PbO \cdot PbSO_4$ plus some $PbSO_4 \cdot Pb_3(PO_4)$, and $Pb_5(OH,X)(PO_4)_3$.

$4PbO \cdot PbSO_4$ was also found in Run #17 along with $Pb_5OH(PO_4)_3$ and lead chlorobromide.

The x-ray diffraction method is capable of identifying only the crystalline species so there is some question whether any non-crystalline species are present which would not be detected. A summary of x-ray diffraction data is presented in Table 17.

TABLE 17

X-RAY DIFFRACTION DATA

Run#	Fuel	Crystalline Species Present
8	Indolene HO 0 +3 ml/gal TEL +It EDB	$PbBr_2$ UP 1875* Chief constituent on Andersen Plate 6 and Filter
9	Indolene HO 0 + 3 ml/gal TEL + 1t EDC	$PbCl_2$ UP 1875 (high Cl) and 5-10% $PbCl_2$ on Andersen Plate 6 UP 1875 only, Filter
11	Indolene HO 30	Pb $(Cl, Br)_2$ UP 1875 present (20-30%) on Andersen Plate 6 and Filter
12	11, cycled	Pb $(Cl, Br)_2$ UP 1875 5-10% to 10-20% from Andersen Plate 1 to Filter.
13	Indolene HO 30 + DMA-4A	Pb $(Cl, Br)_2$ UP1875 10-20% on Andersen Plate 6 and 20-30% on Filter
14	Indolene HO 30+ DMA-4A cycled	Pb $(Cl, Br)_2$ UP 1875 50% on Andersen Plate 6 and 30-40% on Filter

*UP 1875 - Unidentified Pb-Cl-Br structure.

15	Blank (Diluent Air)	Quartz Calcite NaCl NH_4Cl all weak lines
16	Indolene HO 0	Pb (Cl, Br)$_2$ NH_4Cl Pb_5 OH $(PO_4)_3$
17	16, cycled	Pb (Cl, Br)$_2$ NH_4Cl Pb_5 OH $(PO_4)_3$ 4PbO·Pb SO_4 (trace)

4. Transmission Electron Microscopy Characterization - (Penn Schloemann)

The purpose of this work using the transmission electron microscope is to characterize the particles smaller than one micron and obtain crystallographic analysis of the particles by means of electron diffraction.

The electron photomicrographs and diffraction patterns were made from the exhaust particles collected on electron microscope grids. The grids were placed on Andersen Sampler collection plates 1, 3, and 6 and on the Millipore filter. Usually no mounds or impingement points appeared on the grids, so that the photomicrographs represent the area between these points. The particles documented range in size from 100 to 1000Å. Sometimes a particle as large as 10 microns is shown.

Besides the importance of documenting the small particle, the transmission electron photomicrographs show the difference and similarity in particle character among the runs and also between the runs and the blanks. For example, Blank Run #15 appears to be the most different of all the runs. The particles seen in Runs 12 and 13 seem to be the most alike of any runs.

Run 9 was picked to study the electron grids for the presence of organic particles. A photomicrograph was made and then the grid was washed in the hot vapors of hexane and the same, or a similar, area was photographed again. The only difference observed appeared on plate 6 where some of the small particles next to a large one were dissolved away.

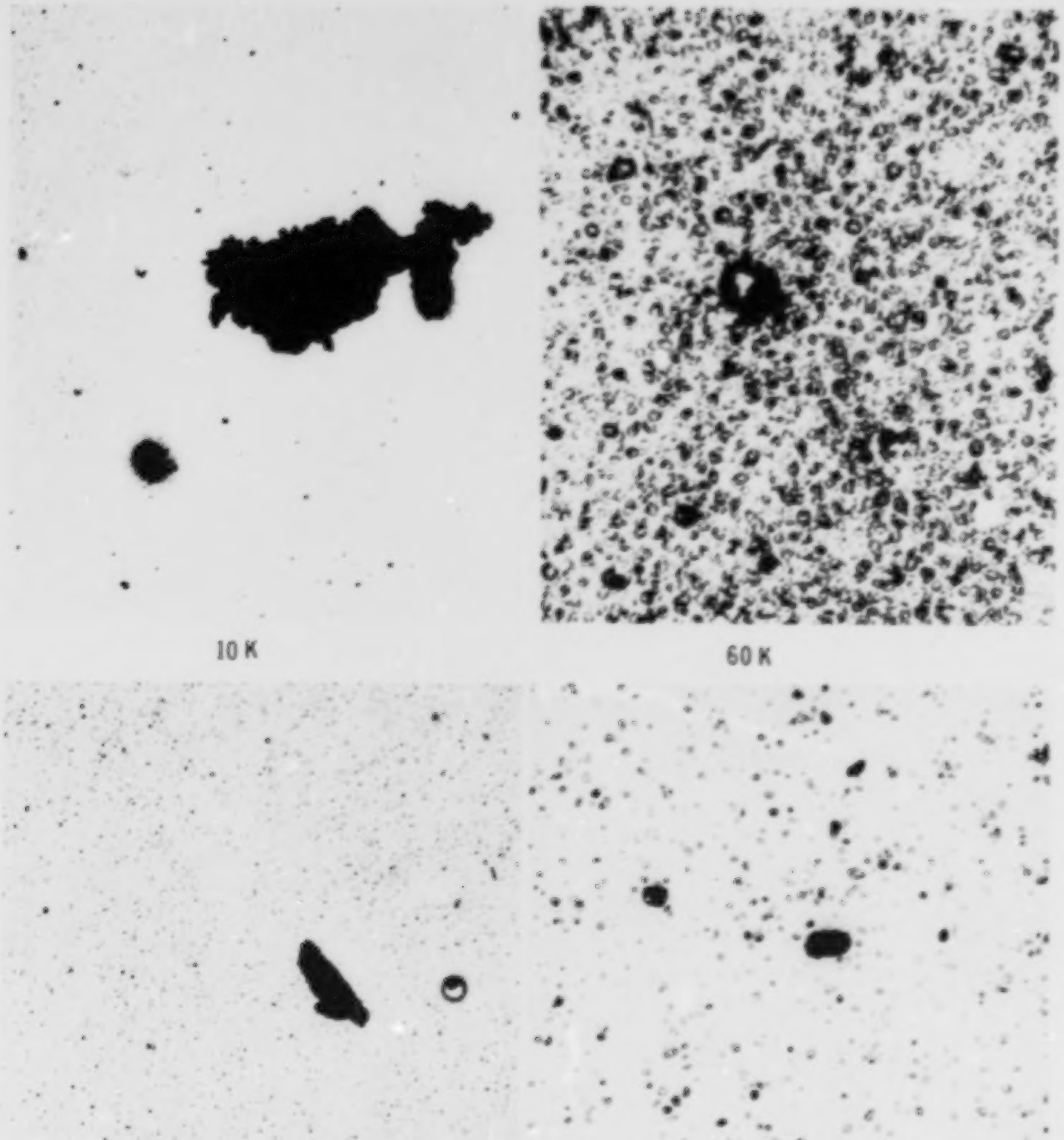
Sometimes the particles undergo a change in appearance from black to white under the electron beam. This is shown in photos of Run 12, Plate 1, (top, Figure 49). The exact change taking place is not known, but electron diffraction patterns show a slightly different compound to be present after the change.

This has been the progress of the transmission electron work thus far: (1) to document the particles, (2) to compare the particles in each run, and (3) to note any peculiarities in the sample. Progress has also been made in the area of electron diffraction analysis.

Figures 47 through 50 are examples of the photomicrograph for runs 9 and 12 as follows:

Figure 47:	Run #9	Plate 1 - top half Plate 3 - bottom half 10,000 and 60,000X
Figure 48:	Run #9	Plate 6 - top half Filter - bottom half 10,000 and 60,000X
Figure 49:	Run #12	Plate 1 - top half Plate 3 - bottom half 10,000 and 60,000X
Figure 50:	Run #12	Plate 6 - top half Filter - bottom half 10,000 and 60,000X

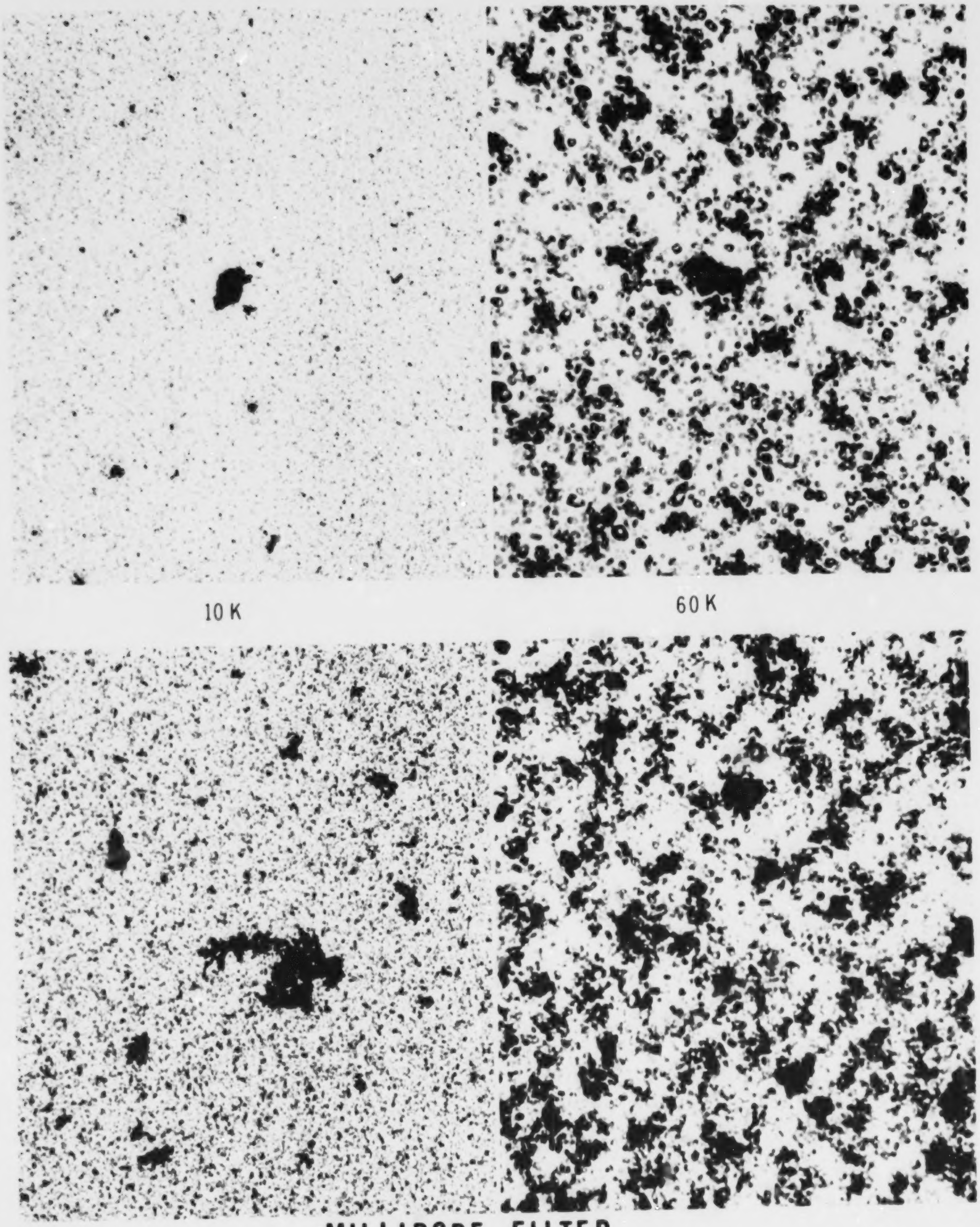
Figure 47



10 K

60 K

Figure 48



10K

60K

MILLIPORE FILTER

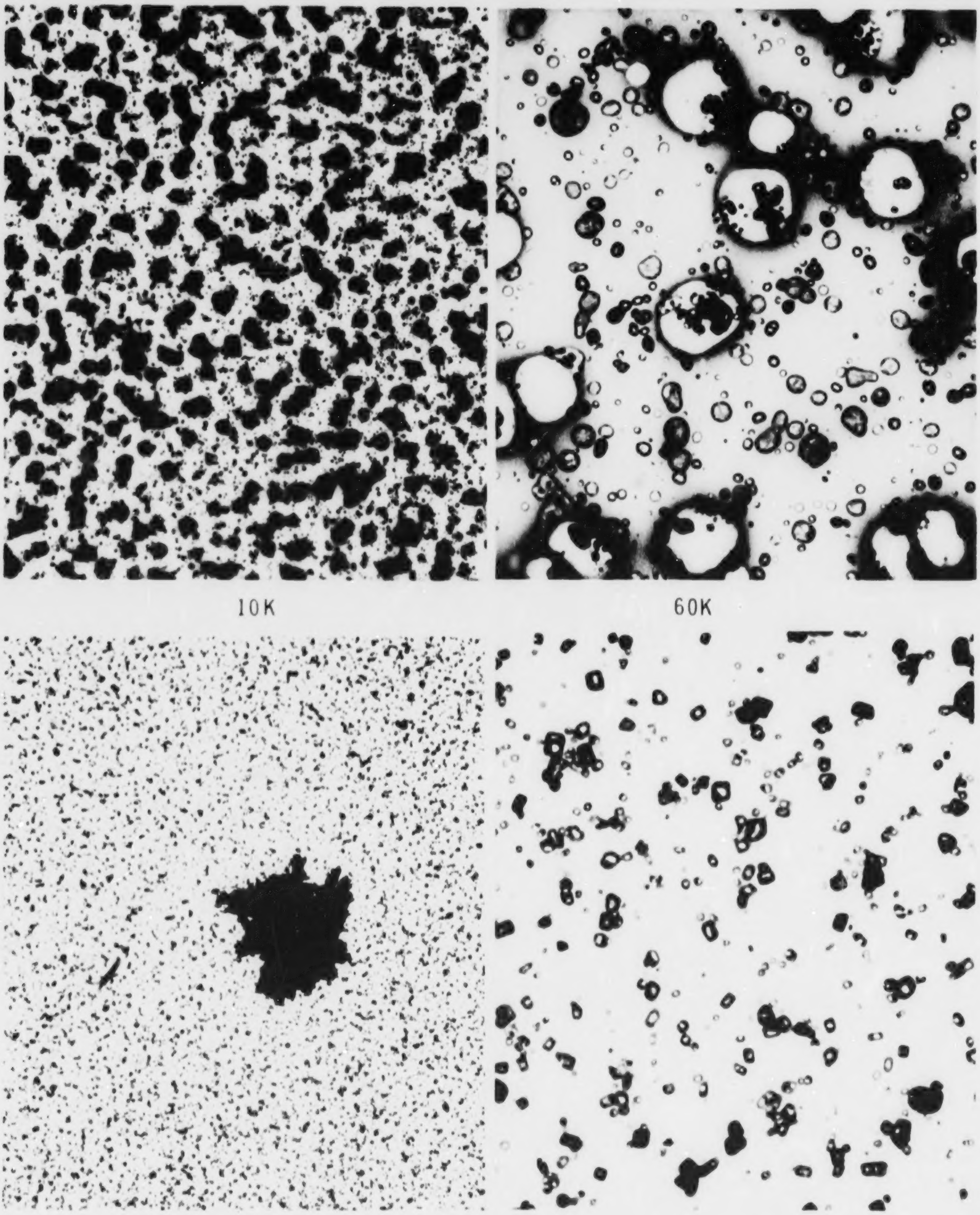
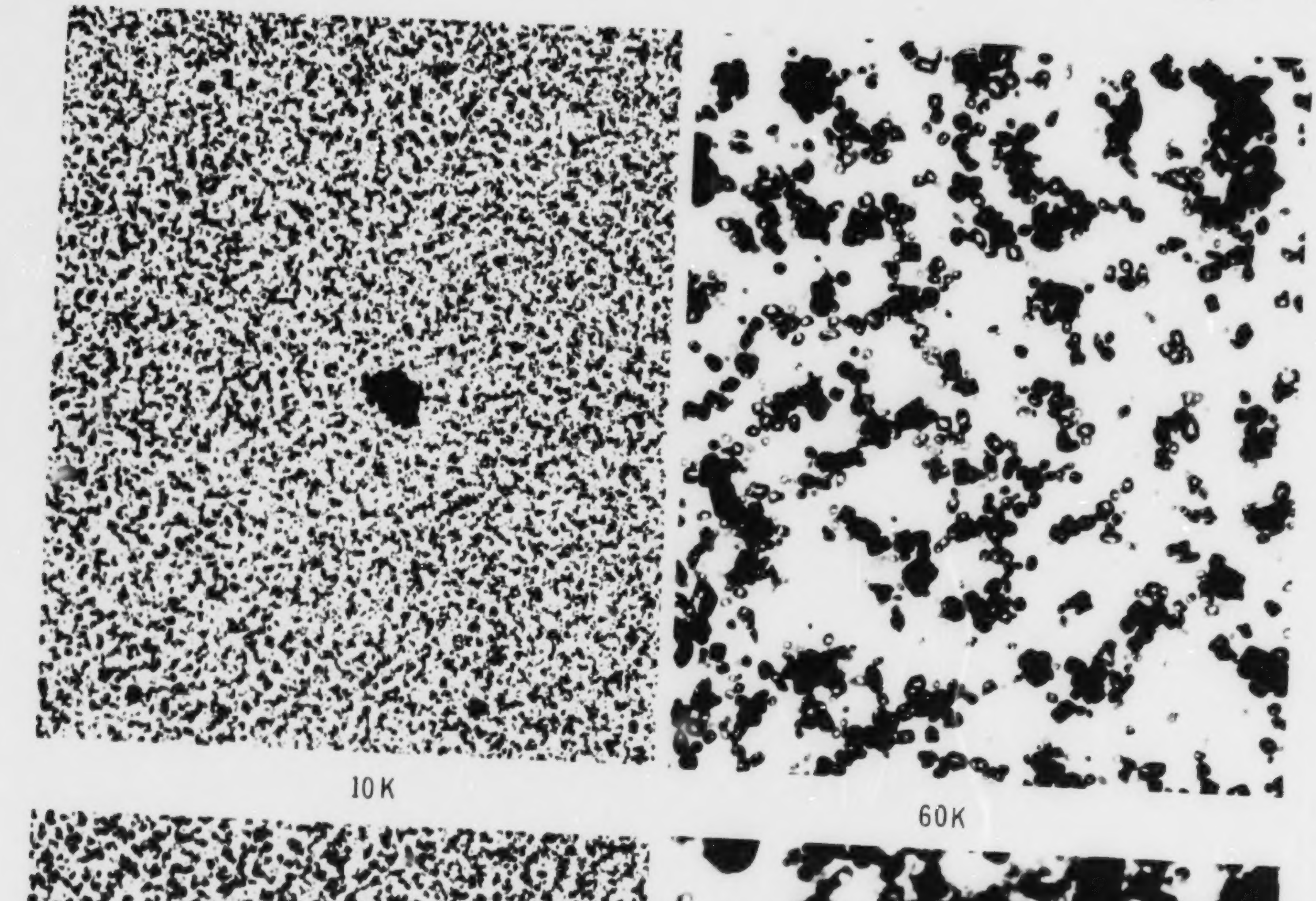


Figure 49

10K

60K

Figure 50



10K

60K

MILLIPORE FILTER

H. MASS SPECTROMETRIC ANALYSIS - (J. C. Tou)

Mass spectrometry was used in this project for the semi-quantitative and qualitative comparison of the levels of NH_3, H_2O, HCl, and organics on the auto exhaust particulates obtained from an engine using different types of fuels and fuel additives and under different operating conditions. Different mass spectrometric techniques were tried and their advantages and disadvantages are discussed in this section.

The mass spectra were obtained at 70 ev using a standard 90° magnetic sector mass spectrometer. The sample was scraped from the trays of the Andersen Sampler, weighed and devolatilized in a 500 cc reservoir. The vapors were introduced into the ion source through a 2 mil diameter molecular leak while the inlet system was held at 200°C. In an attempt to avoid the changes in the composition during sampling, the scans were delayed one minute to assure complete volatilization of organics. Both the masses and the intensities of peaks were digitized automatically during scanning of the mass spectrum. A low energy (~10 ev, uncalibrated) mass spectrum of one sample showed the presence of intense peaks at m/e=17, 18 and 36 which could be due to NH_3, H_2O, and HCl. These tentative identifications were extended to other samples.

Assuming that the average instrumental sensitivity for the components in the sample remained approximately constant between samples, the following quantities were calculated as a measure of the relative amounts of NH_3, H_2O, HCl and organics respectively.

$$\left[\frac{I_{17} - 0.21\, I_{18}}{W \times S_t}\right] NH_3, \qquad \left[\frac{I_{18}}{W \times S_t}\right] H_2O$$

$$\left[\frac{I_{36}}{W \times S_t}\right] HCl \qquad \text{and} \qquad \left[\frac{\sum\limits_{i = 40}^{200} I_i}{W \times S_t}\right] \text{Organics}$$

where I_i is the intensity of the peaks at $m/e = i$, W the weight in mg of sample loaded, S_t the toluene sensitivity of the mass spectrometer on the day when the samples were run.

The term $0.21\ I_{18}$ in the case of NH_3 was introduced to correct for the contribution of the fragment ion HO^+ from H_2O to the intensity of the peak at $m/e = 17$. The mass spectral profile of organics in the auto exhaust particulates was plotted using a B-5500 computer by connecting the mass to charge peak tops after the intensities of the peaks had been normalized by the computer according to the following formula:

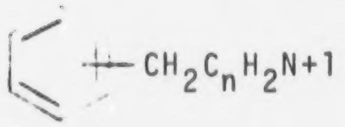
$$\frac{I_i}{\sum_{j=25}^{250} I_j}$$

$$j \neq 28, 32, 44, 36, 38$$

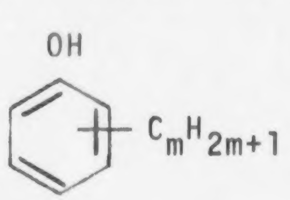
Plots were made of the data for those spectra with enough intensity to be judged significant. The plotted profiles allow one to make a direct comparison of the relative changes in organic composition for the samples obtained at different engine conditions.

The direct probe sample introduction technique was also used in the characterization of the particulates. This technique allows the sample to be heated up to 600°C in a miniature oven located a few mm away from the electron beam in the mass spectrometer. The mass spectra were taken at different temperatures of the oven and shows the presence of PbClBr, $PbBr_2$ and organic components giving peaks at m/e = 43, 55, 57, 69, 71, et al. However, the technique did not allow one to observe the differences between samples.

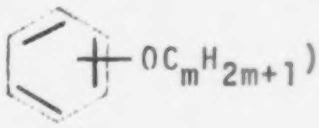
A combination technique of direct probe and field ionization mass spectrometry was also tried. Field ionization mass spectrometry is a technique of ionizing the molecules with a high electric field in the order of 0.1v/Å. This is a much milder means of ionization than electron impact. Hence, the fragmentation of a molecular ion is very much reduced in the field ionization mass spectrum and thus the spectral features are simplified. The field ionization mass spectra of only one sample were obtained using a CH4B mass spectrometer and these were weak and complex. However, peaks 14 masses apart are clearly shown in some of the spectra. Two series of peaks were observed: a) m/e = 92 + 14xn, where n=0-6 or higher, b) m/e = 94 + 14xm, where m=0-4 or higher, which might be due to the molecular ions of:



and



(or



)

respectively. The disadvantage of not being able to observe the difference between samples involved in the direct probe technique for characterizing the particulates also remains in this approach.

High resolution mass spectrometry was also used in this study to find the accurate masses of the ions observed in the mass spectrum within an accuracy of 5 millimass units. The accurate masses were used for the calculation of the elementary compositions of the ions which should reflect the composition of the sample to some extent. The high resolution mass spectrum was recorded on a photo plate by using a CEC 110B high resolution mass spectrometer. The data were processed with use of a Grand-Datex photo plate reader and a B-5500 computer.

It was found that the data obtained were extremely complex and difficult to interpret. However, the hydrocarbon ions were clearly shown in the high resolution mass spectrometric data.

Table 18, as an example, indicates the relative values for NH_3, H_2O, HCl, and organic level corrected for instrument sensitivity for run 4 for samples scraped from the plates of the Andersen Sampler and from the filter, and samples collected from the dilution tube slit plates. The data for each Andersen plate and filter for each test fuel is shown graphically in Figures 51 through 63. Figures 64 through 72 are examples of the calculated and computer plotted mass spectral profiles for run #11 (Indolene HO 30) and run #16 (Indolene HO 0).

The less the amount of sample available, the less accurate the calculated data are. It was noted that the samples scraped from the fiberglass filters were contaminated with filter fiberglass. Hence, the calculated values on Table 18 for the filter samples are not accurate and represent the lower limit. Care should be taken in the interpretation of the data. The mass spectral profiles of the filter samples, however, will not be affected by the presence of fiberglass.

Generally speaking, the organic levels increase as the number of the Andersen plate increases for a particular run. Also found was that the organic levels of slit samples were lower than those of samples collected on the Andersen Sampler.

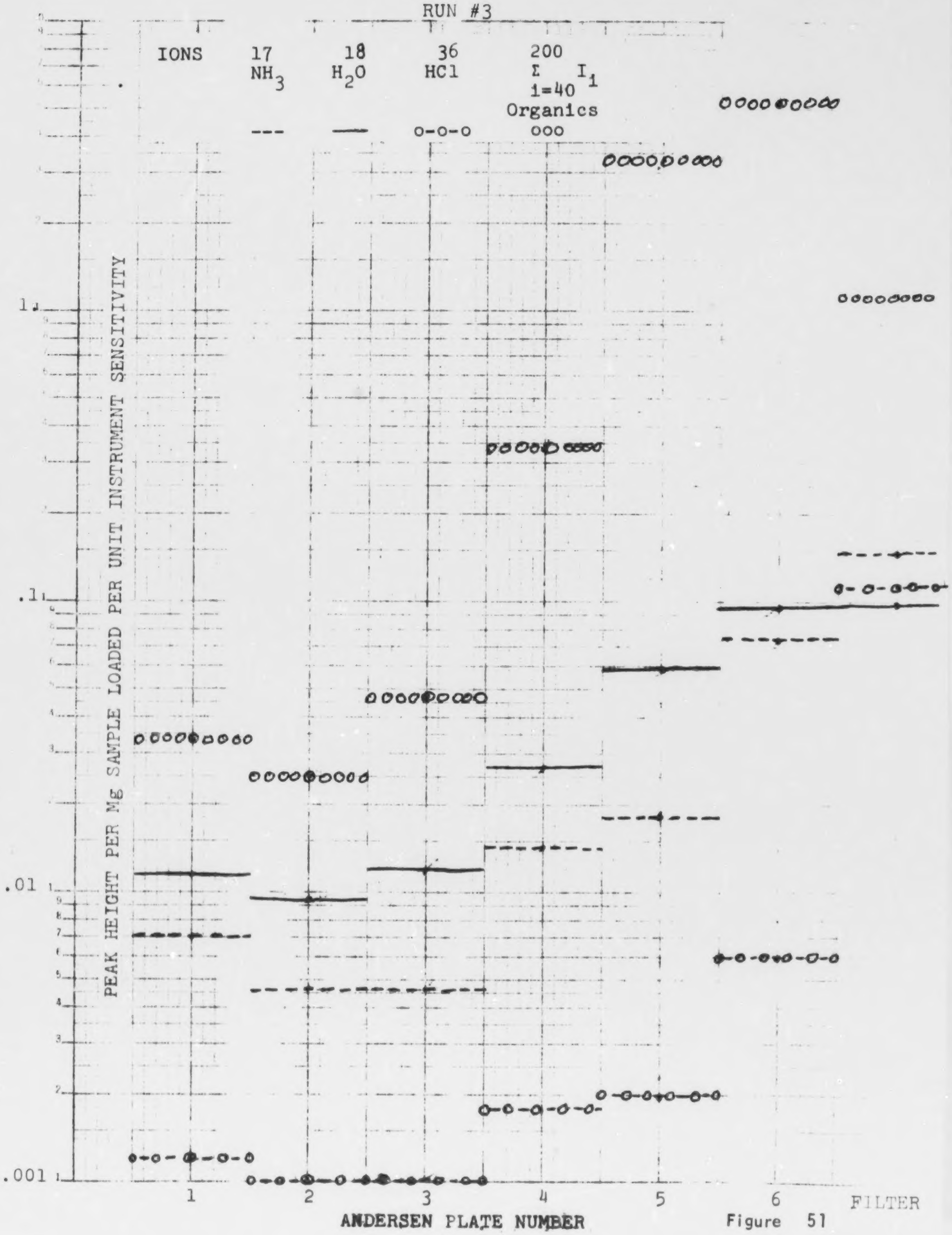

RUN #3
IONS
17 NH3 ---
18 H2O —
36 HCl o-o-o
200 Σ i=40 Ii Organics ooo
PEAK HEIGHT PER Mg SAMPLE LOADED PER UNIT INSTRUMENT SENSITIVITY
1
.1
.01
.001
1
2
3
4
5
6
FILTER
ANDERSEN PLATE NUMBER

Figure 51

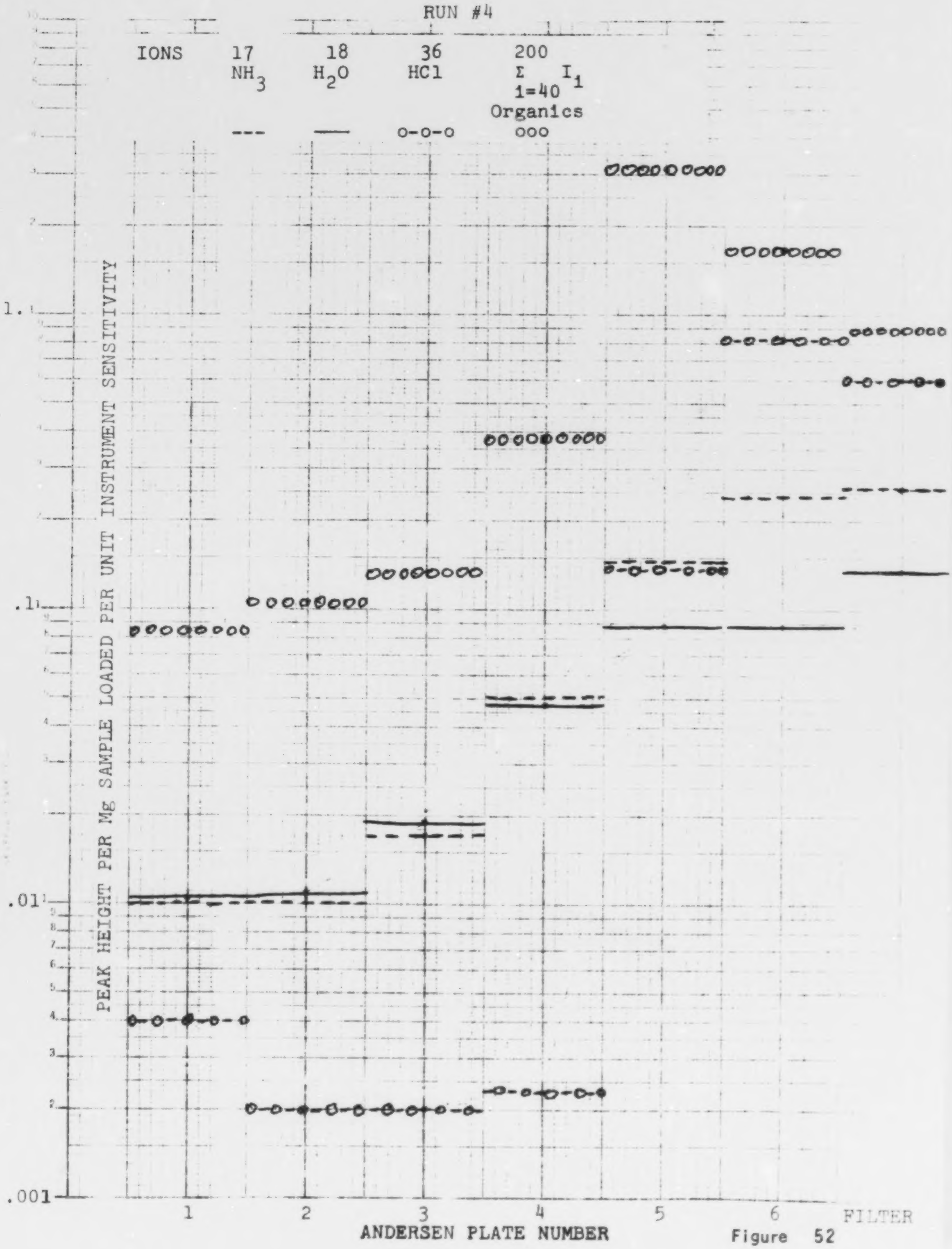

RUN #4
IONS
17 NH_3 ---
18 H_2O —
36 HCl o-o-o
200 $\Sigma_{1=40} I_1$ Organics ooo
PEAK HEIGHT PER Mg SAMPLE LOADED PER UNIT INSTRUMENT SENSITIVITY
1.
.1
.01
.001
1
2
3
4
5
6
FILTER
ANDERSEN PLATE NUMBER

Figure 52

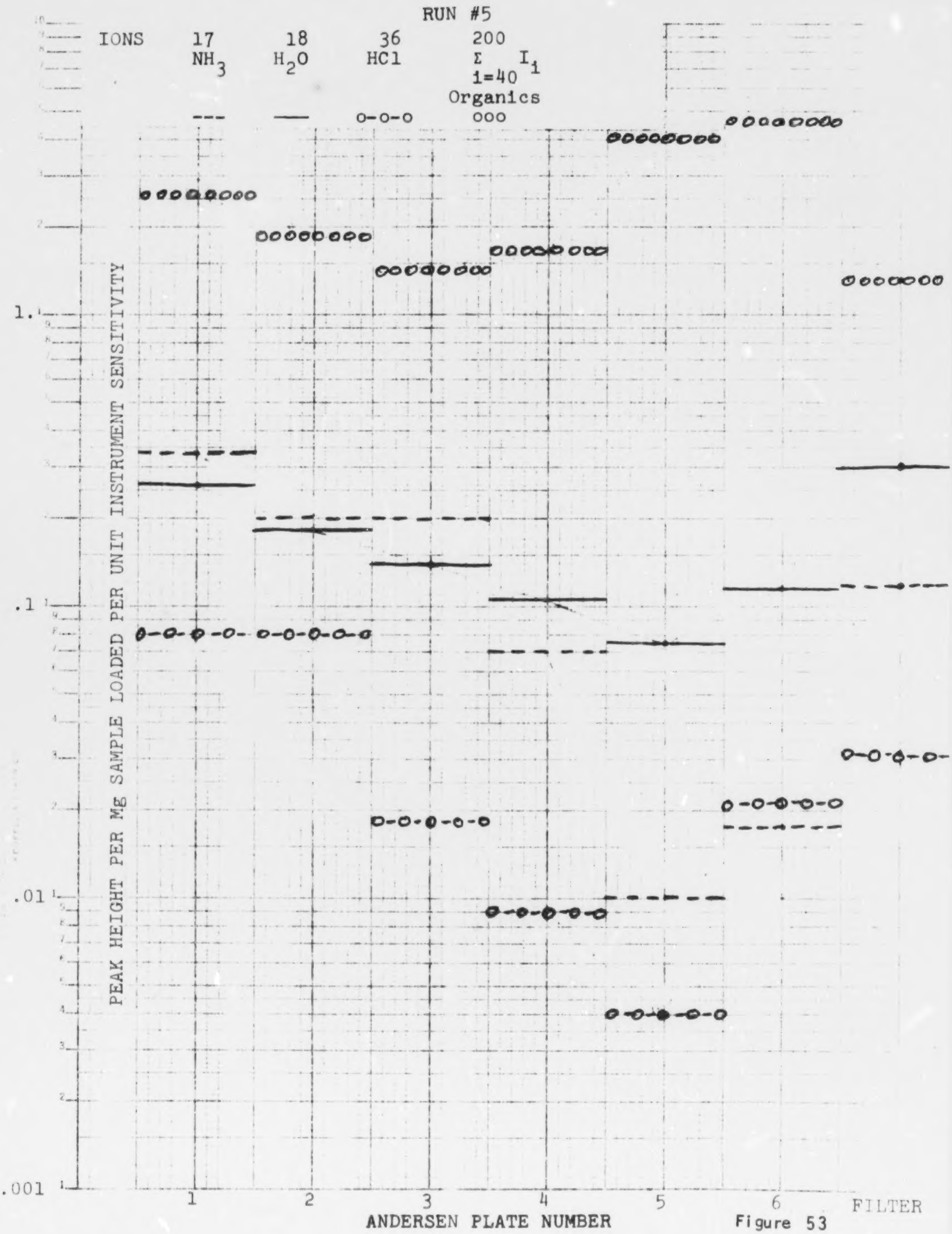

RUN #5
IONS
17 NH3 ---
18 H2O —
36 HCl 0-0-0
200 Σ i=40 I i Organics 000
PEAK HEIGHT PER Mg SAMPLE LOADED PER UNIT INSTRUMENT SENSITIVITY
1.
.1
.01
.001
1
2
3
4
5
6
FILTER
ANDERSEN PLATE NUMBER

Figure 53

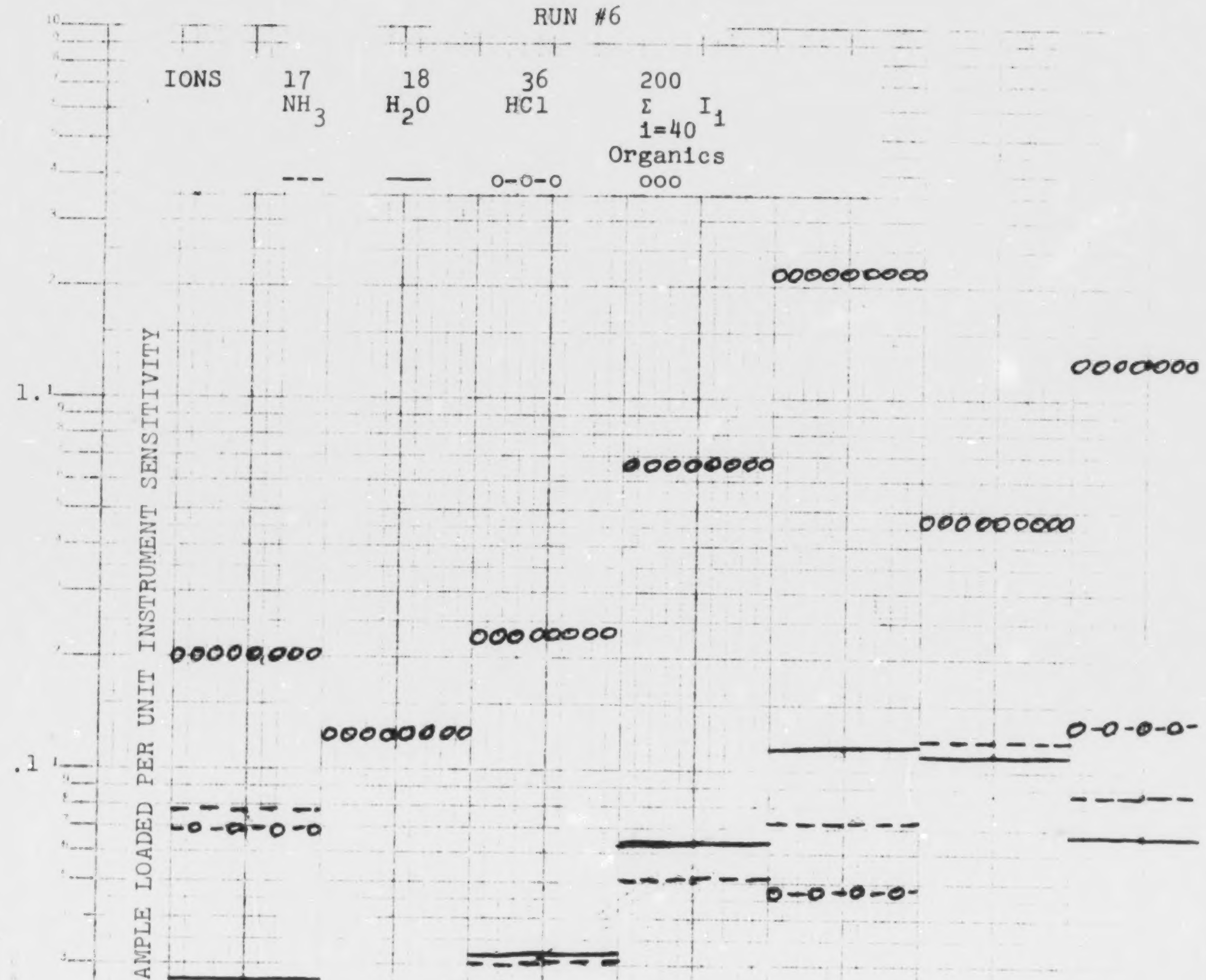
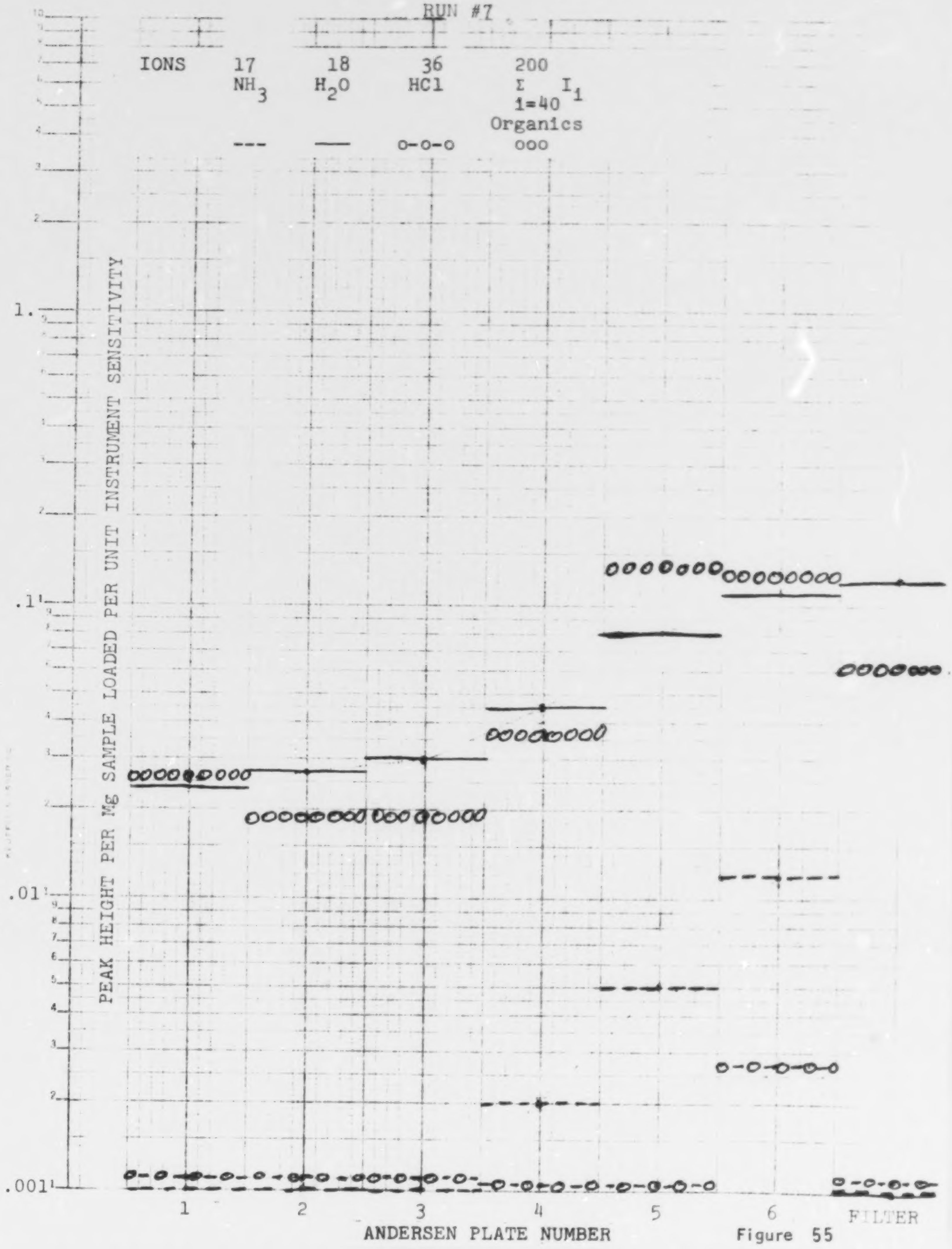

RUN #6
IONS
17 NH3 ---
18 H2O —
36 HCl o-o-o
200 Σ I_i i=40 Organics ooo
PEAK HEIGHT PER Mg SAMPLE LOADED PER UNIT INSTRUMENT SENSITIVITY
1.
.1
.01
.001
1
2
3
4
5
6
FILTER
ANDERSEN PLATE NUMBER

Figure 54


RUN #7
IONS
17
NH3
18
H2O
36
HCl
200
Σ I1
i=40
Organics

——
o-o-o
ooo
1.
.1
.01
.001
PEAK HEIGHT PER Mg SAMPLE LOADED PER UNIT INSTRUMENT SENSITIVITY
1
2
3
4
5
6
FILTER
ANDERSEN PLATE NUMBER

Figure 55

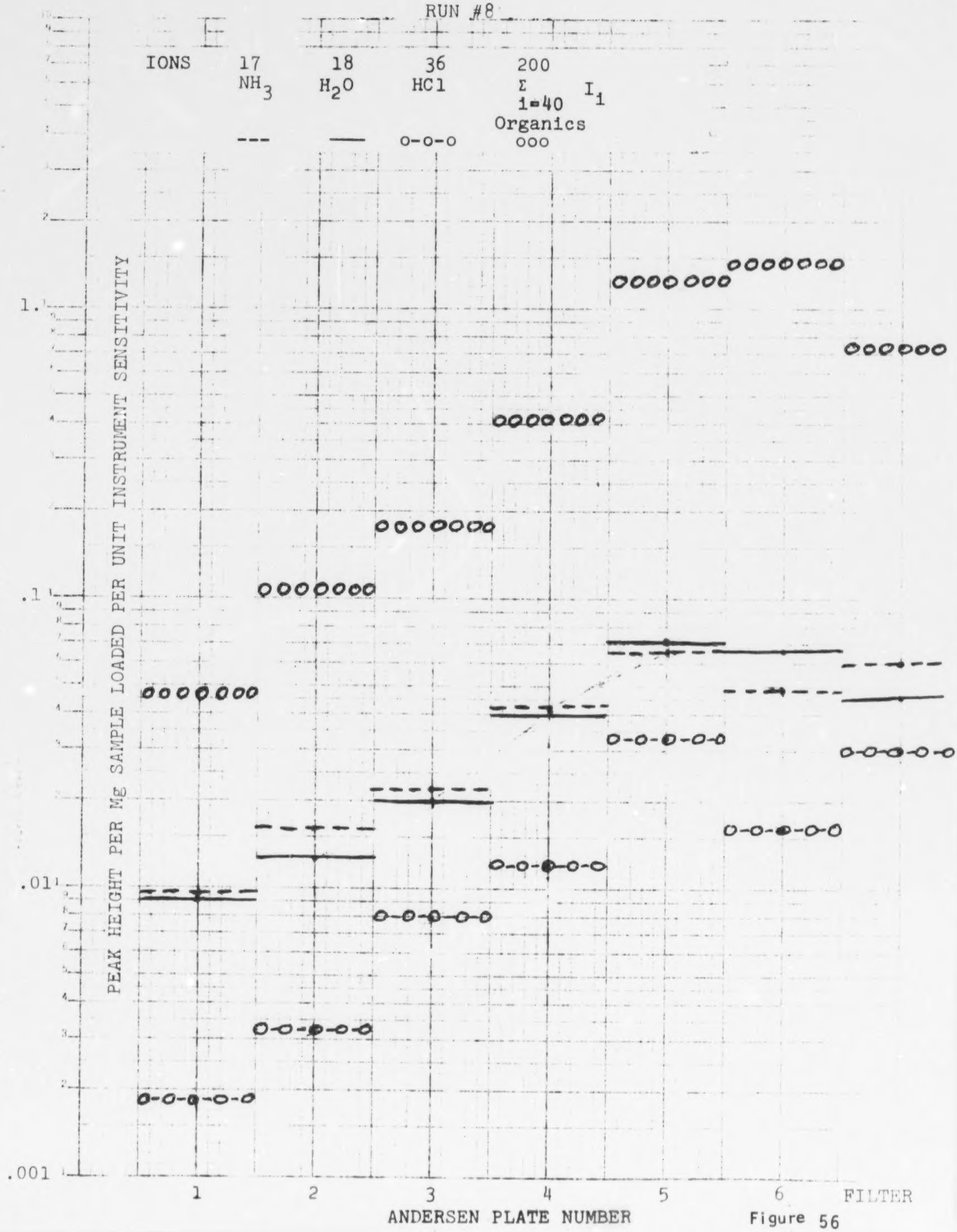

RUN #8
IONS
17 NH3 ---
18 H2O —
36 HCl o-o-o
200 Σ i=40 Organics I_i ooo
PEAK HEIGHT PER Mg SAMPLE LOADED PER UNIT INSTRUMENT SENSITIVITY
1.
.1
.01
.001
1
2
3
4
5
6
FILTER
ANDERSEN PLATE NUMBER

Figure 56

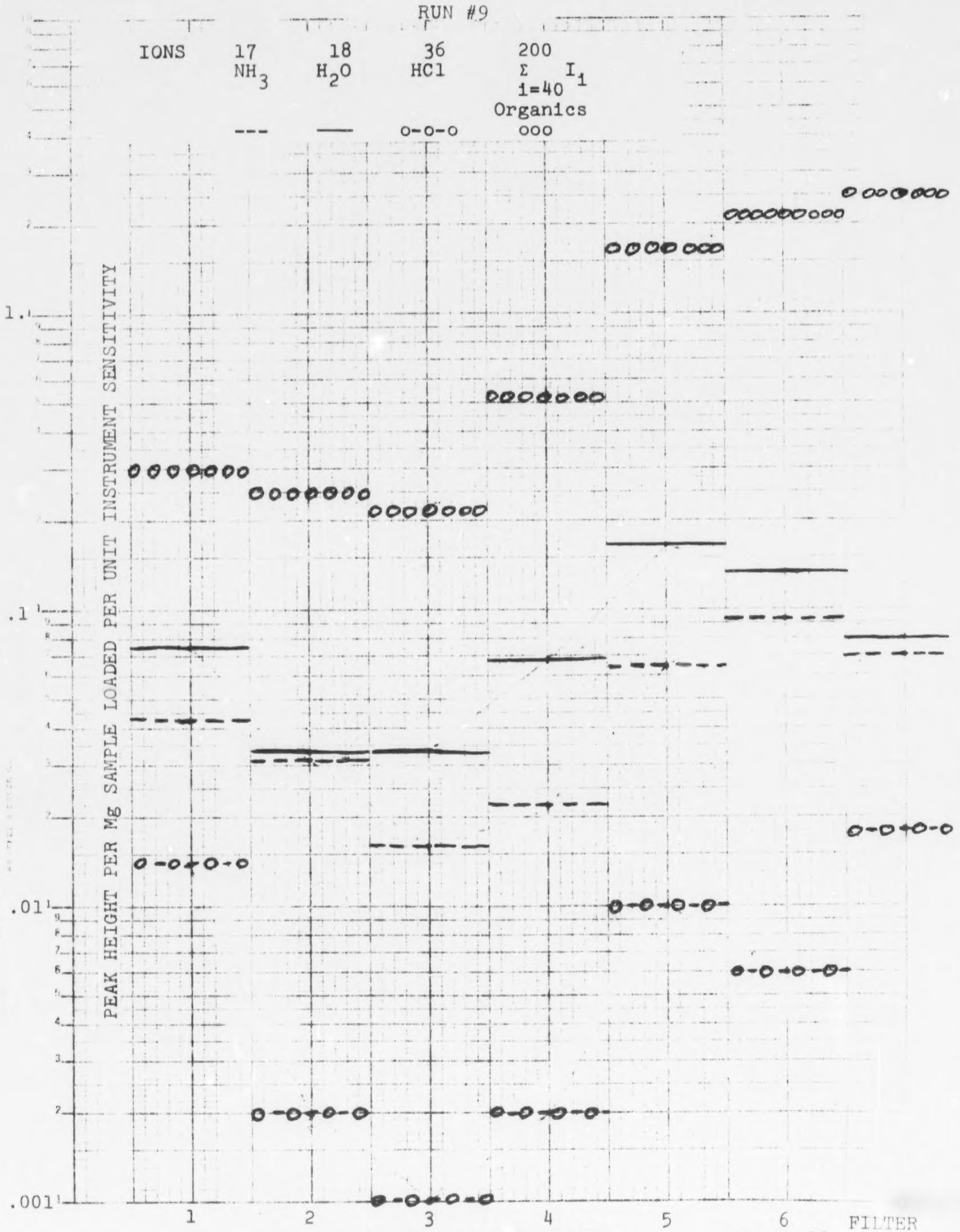

RUN #9
IONS
17 NH_3 ---
18 H_2O ——
36 HCl o-o-o
200 $\sum_{i=40} I_i$ Organics ooo
PEAK HEIGHT PER Mg SAMPLE LOADED PER UNIT INSTRUMENT SENSITIVITY
1.
.1
.01
.001
1
2
3
4
5
6
FILTER
ANDERSEN PLATE NUMBER

Figure 57

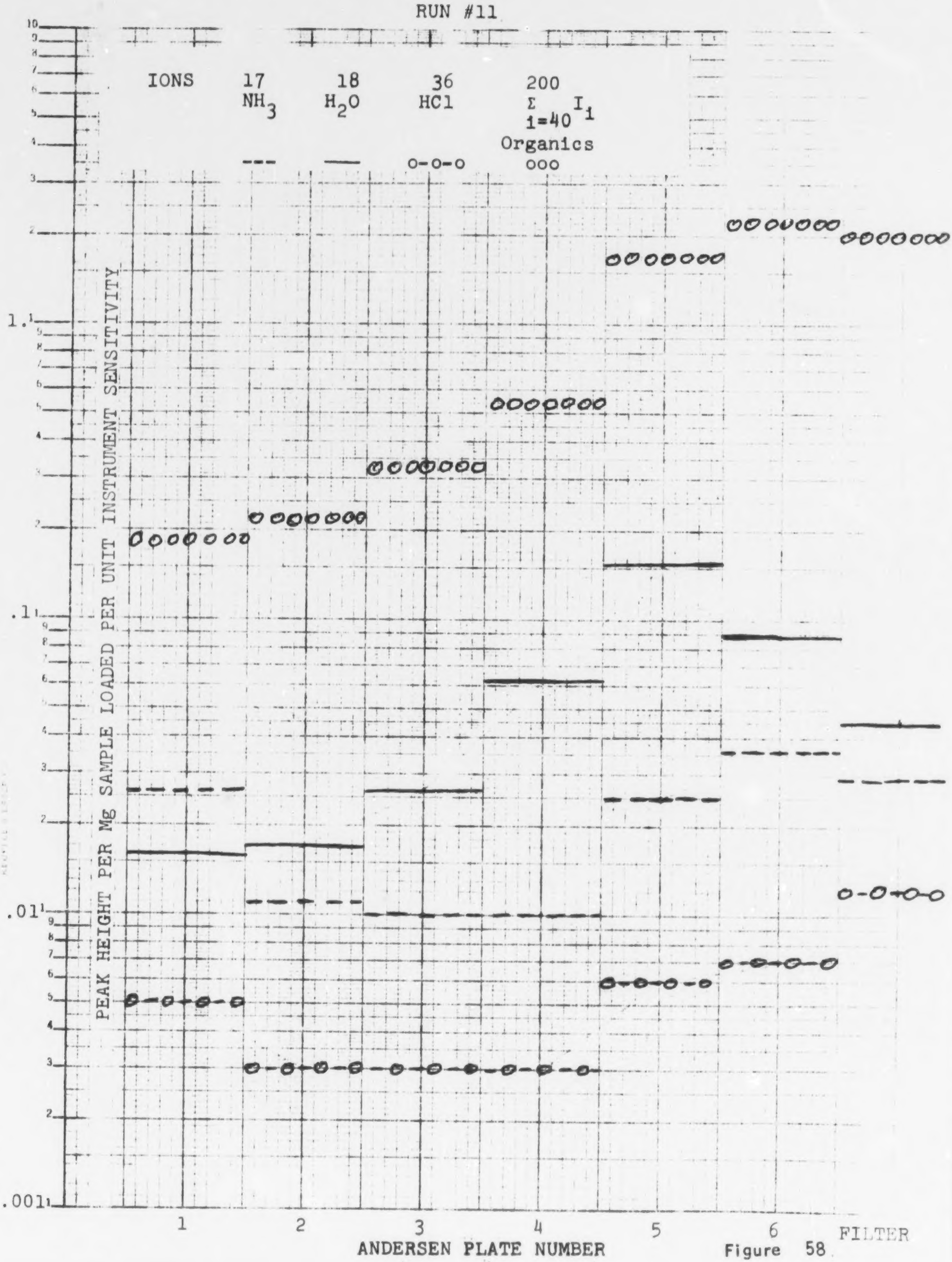

RUN #11
IONS
17 NH3 ---
18 H2O —
36 HCl o-o-o
200 Σ i=40 I1 Organics ooo
PEAK HEIGHT PER Mg SAMPLE LOADED PER UNIT INSTRUMENT SENSITIVITY
1.
.1
.01
.001
1
2
3
4
5
6
FILTER
ANDERSEN PLATE NUMBER

Figure 58

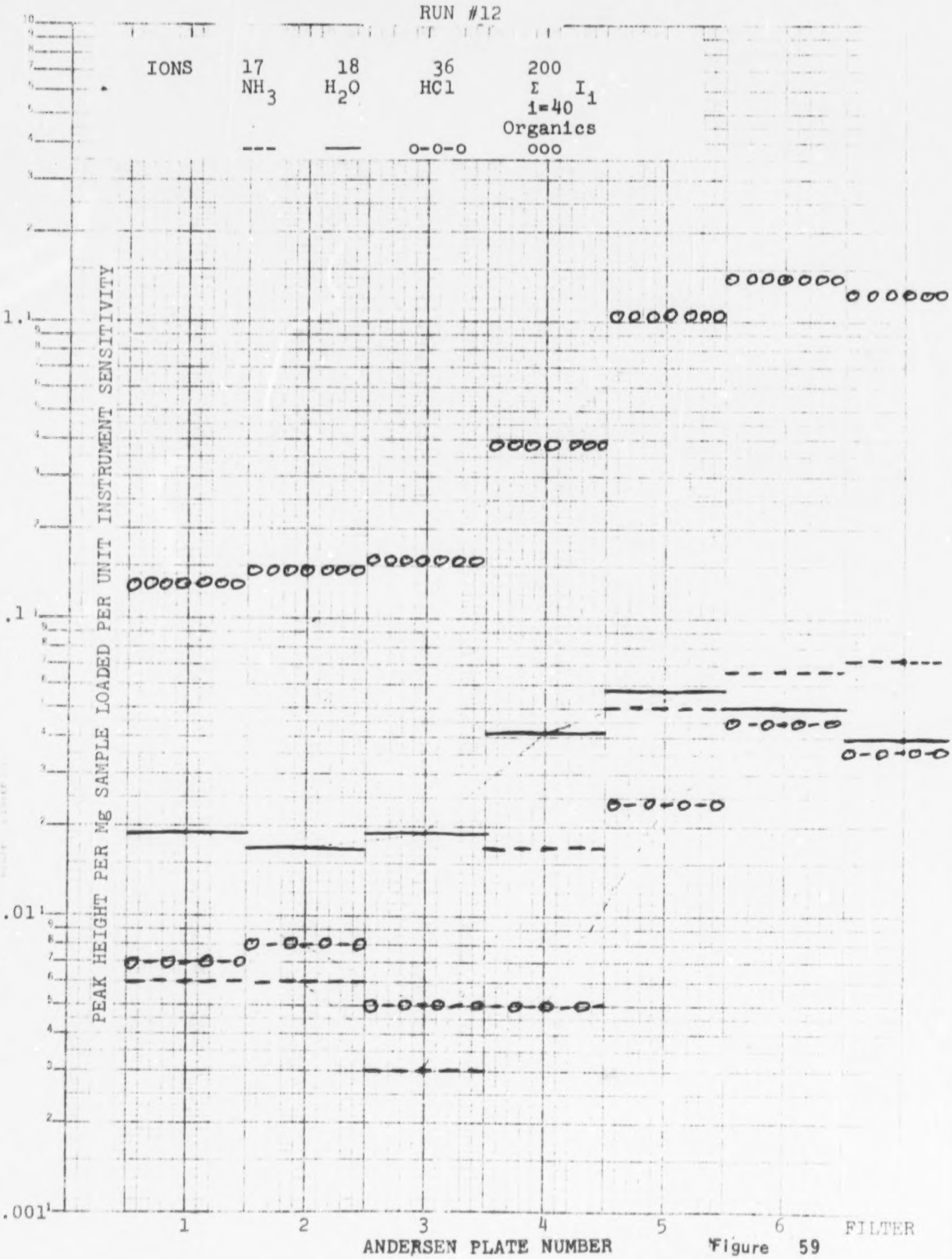
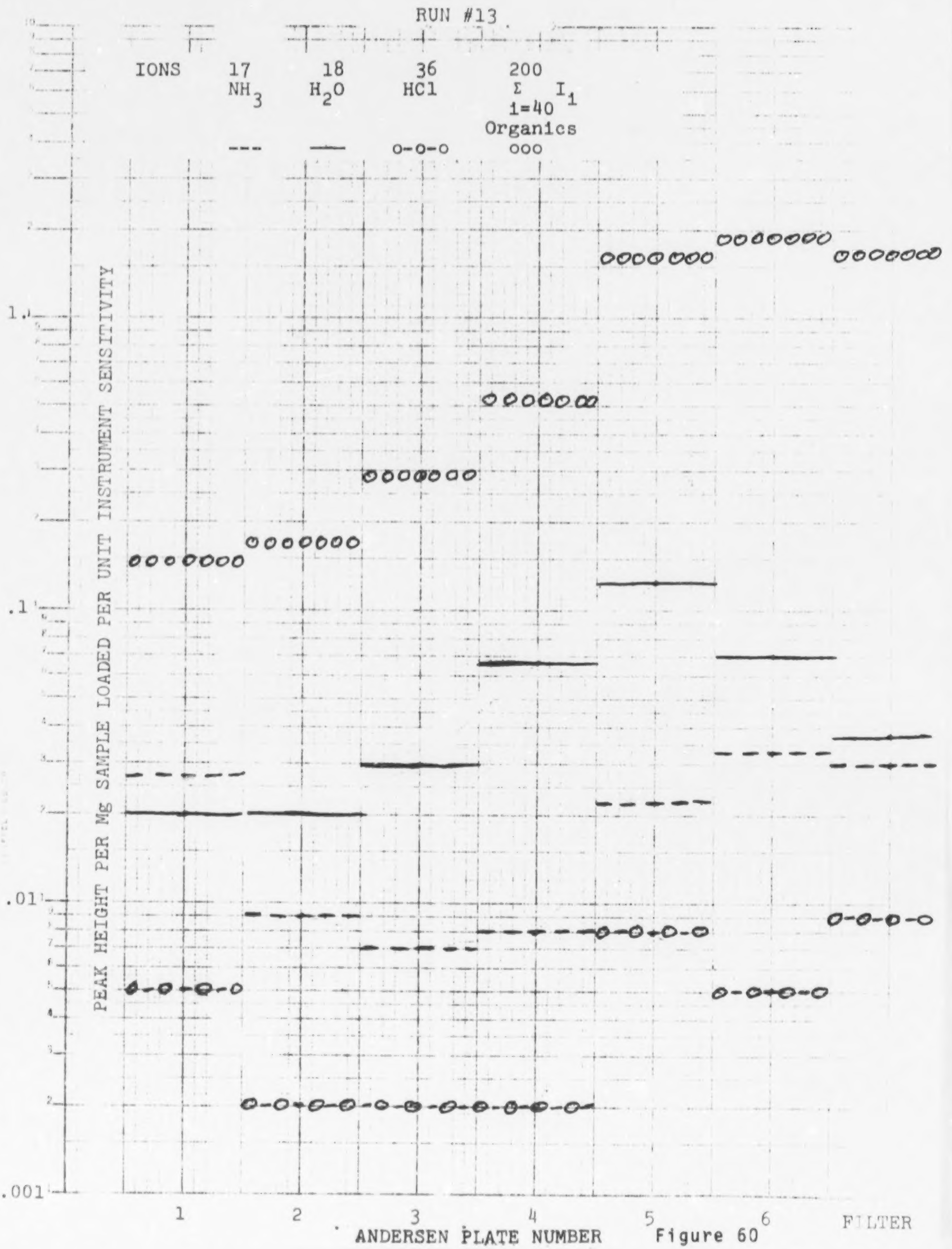
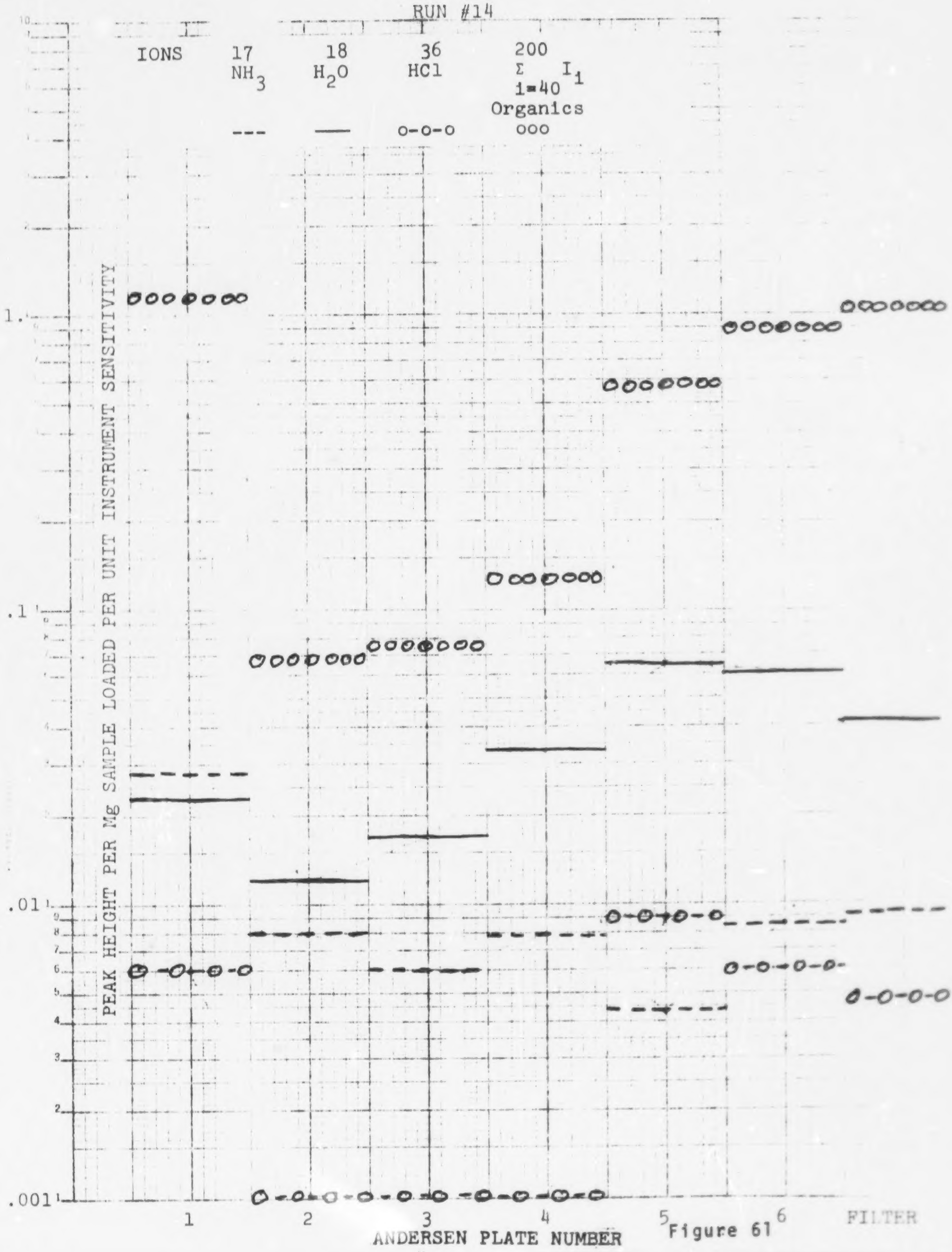

RUN #12
IONS
17 NH3 ---
18 H2O —
36 HCl o-o-o
200 Σ i=1 40 I_i Organics ooo
1.
.1
.01
.001
PEAK HEIGHT PER Mg SAMPLE LOADED PER UNIT INSTRUMENT SENSITIVITY
1
2
3
4
5
6
FILTER
ANDERSEN PLATE NUMBER

Figure 59


RUN #13
IONS
17
NH$_3$

18
H$_2$O
—
36
HCl
o-o-o
200
Σ I$_1$
i=40
Organics
ooo
1.
.1
.01
.001
PEAK HEIGHT PER Mg SAMPLE LOADED PER UNIT INSTRUMENT SENSITIVITY
1
2
3
4
5
6
FILTER
ANDERSEN PLATE NUMBER

Figure 60


RUN #14
IONS
17
NH3
18
H2O
36
HCl
200
Σ I_i
i=40
Organics

——
o-o-o
ooo
PEAK HEIGHT PER Mg SAMPLE LOADED PER UNIT INSTRUMENT SENSITIVITY
1.
.1
.01
.001
1
2
3
4
5
6
FILTER
ANDERSEN PLATE NUMBER

Figure 61

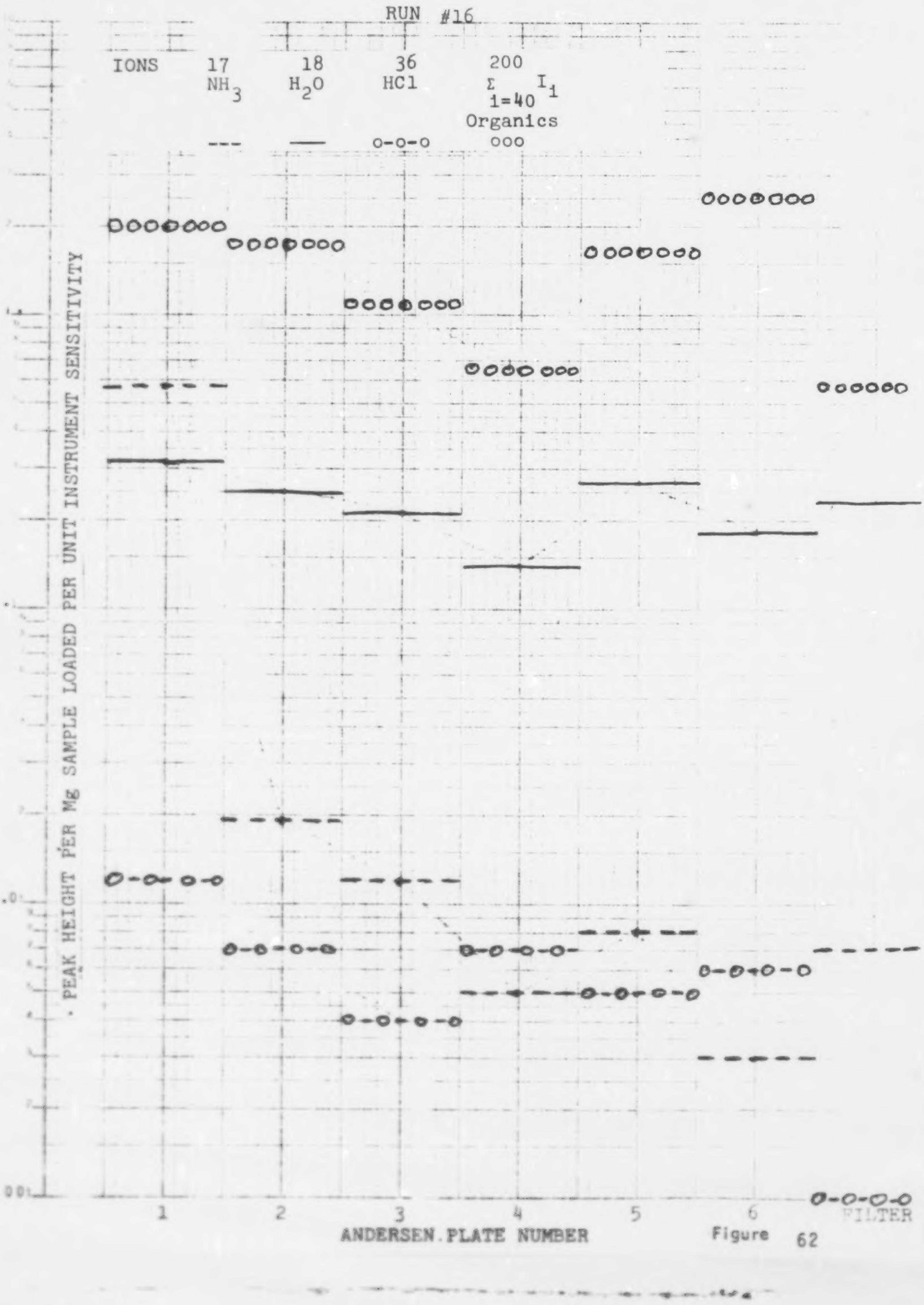

RUN #16
IONS
17 NH3 ---
18 H2O —
36 HCl o-o-o
200 Σ i=40 Ii Organics ooo
PEAK HEIGHT PER Mg SAMPLE LOADED PER UNIT INSTRUMENT SENSITIVITY
.01
.001
1
2
3
4
5
6
FILTER
ANDERSEN PLATE NUMBER

Figure 62

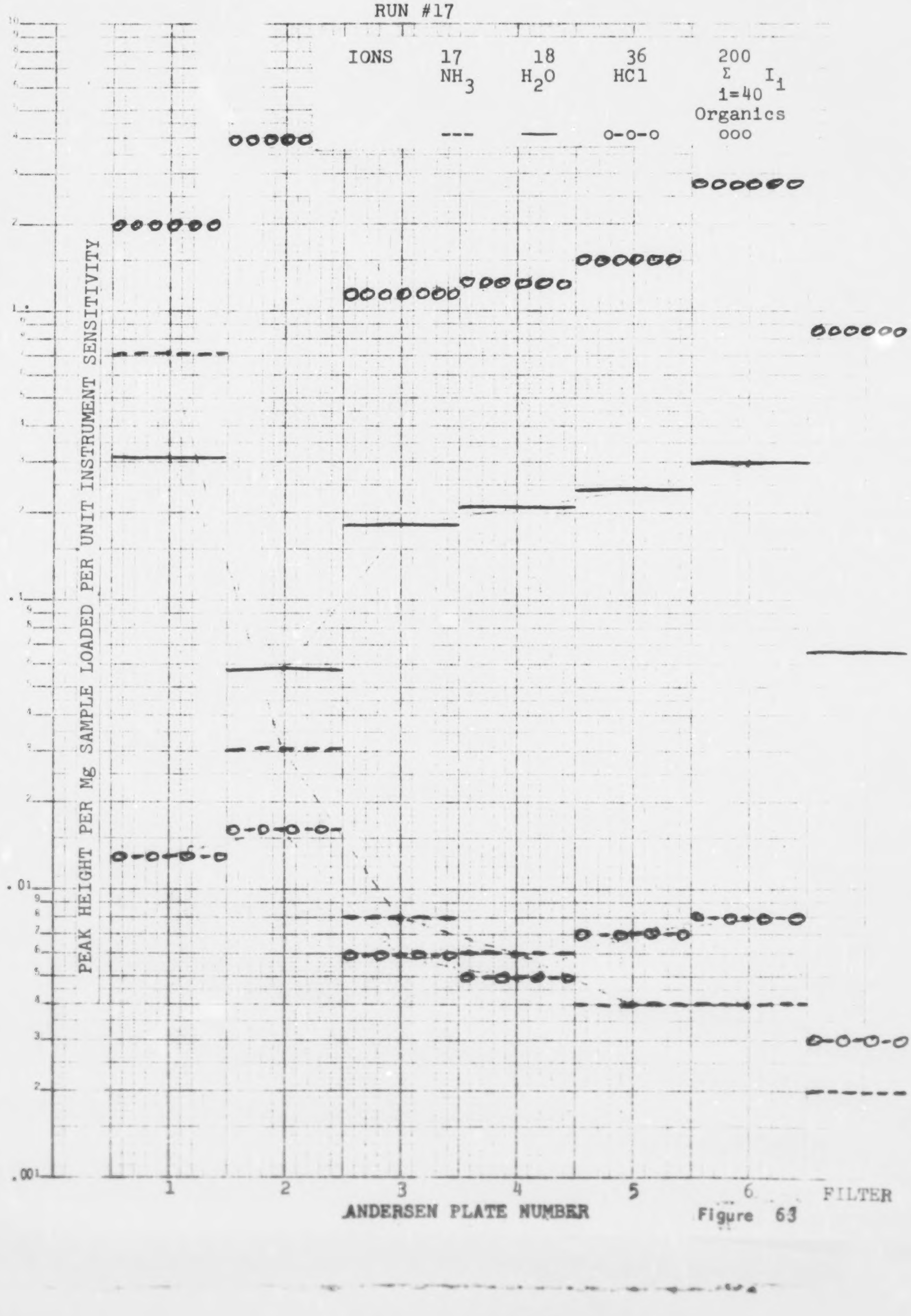
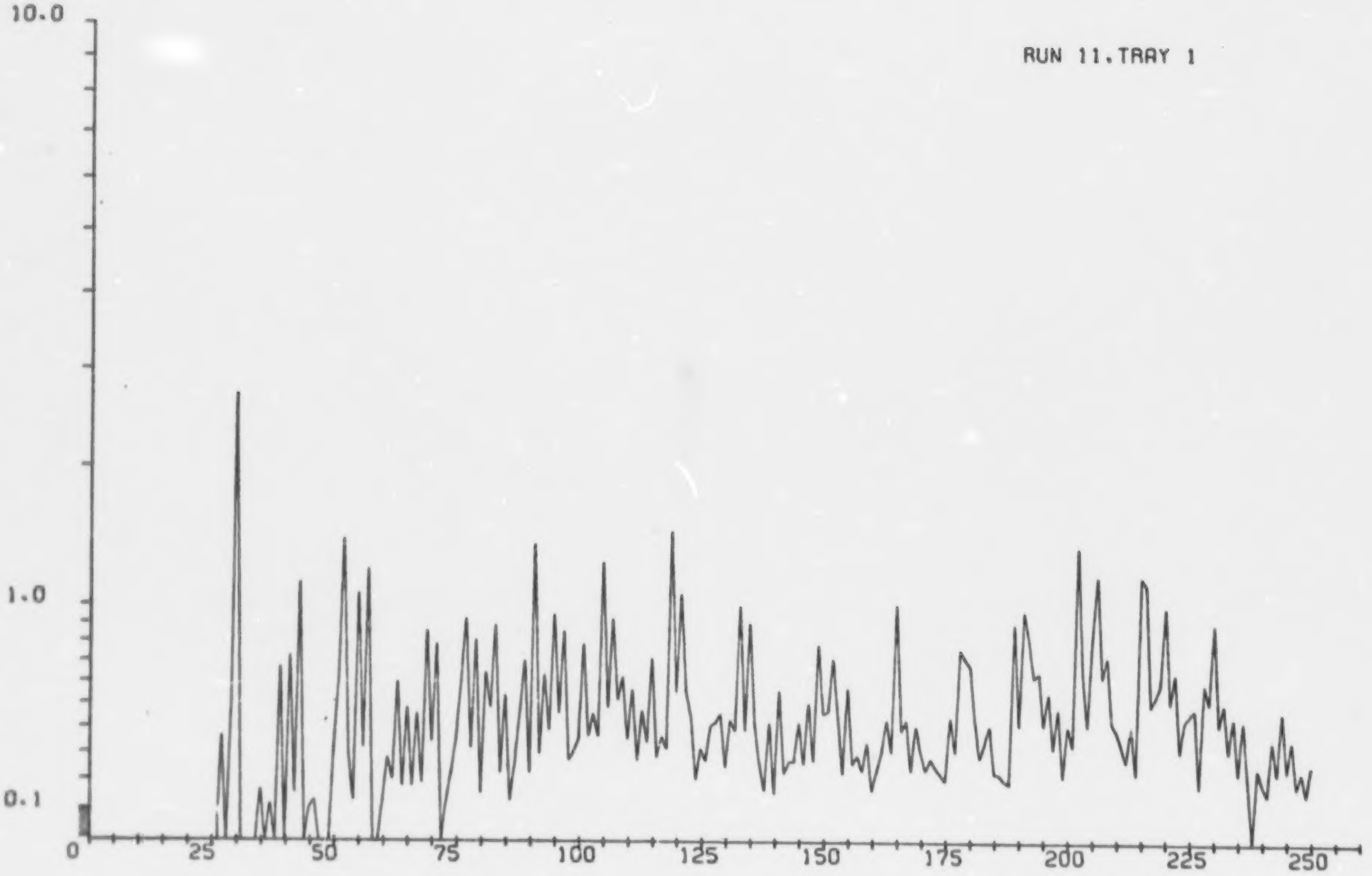

RUN #17
IONS
17 NH3 ---
18 H2O —
36 HCl o-o-o
200 Σ i=40 I_i Organics ooo
PEAK HEIGHT PER Mg SAMPLE LOADED PER UNIT INSTRUMENT SENSITIVITY
1.
.1
.01
.001
1
2
3
4
5
6
FILTER
ANDERSEN PLATE NUMBER

Figure 63



CALIFORNIA COMPUTER PRODUCTS, INC. ANAHEIM, CALIFORNIA CHART NO. 400

Figure 64

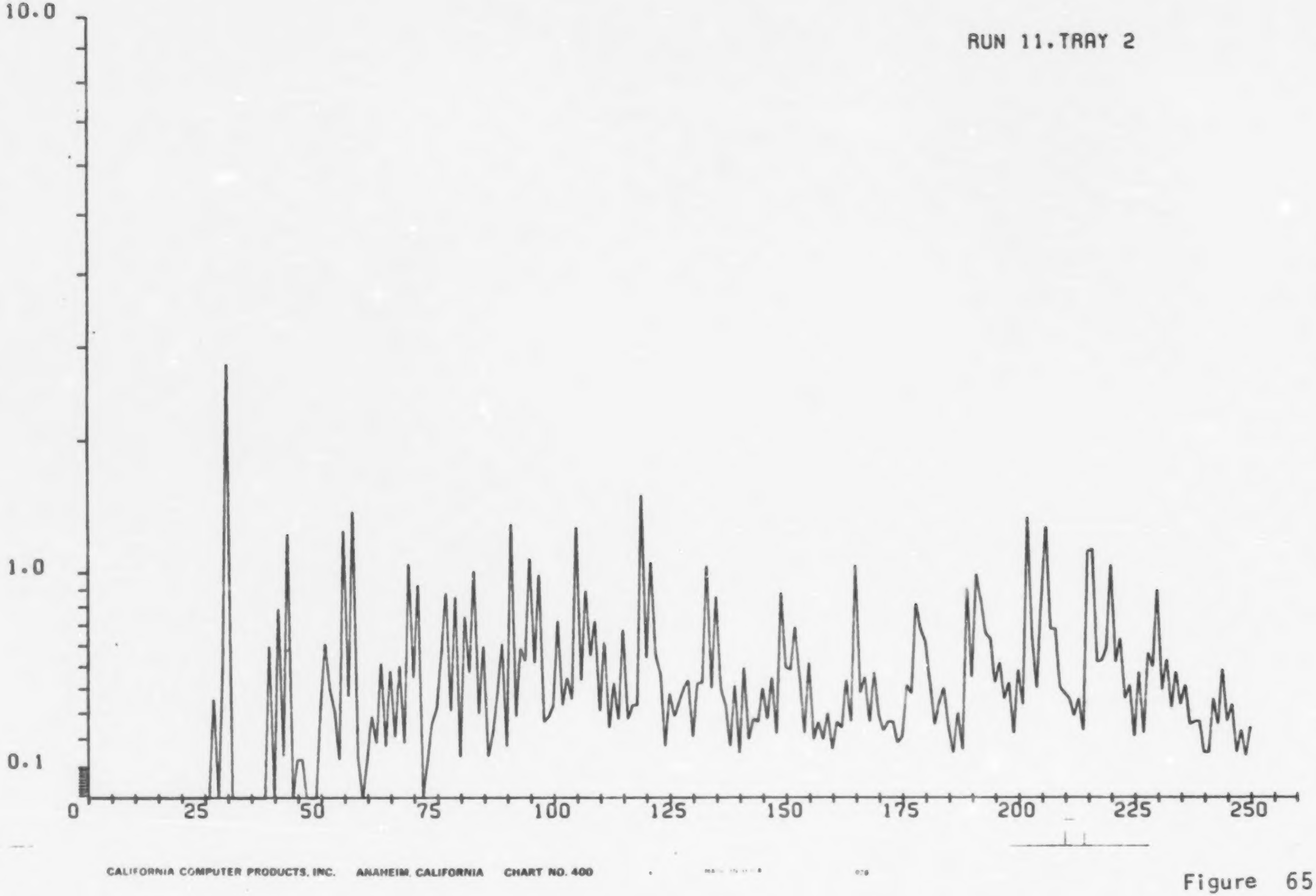

RUN 11.TRAY 2
10.0
1.0
0.1
0
25
50
75
100
125
150
175
200
225
250
CALIFORNIA COMPUTER PRODUCTS, INC. ANAHEIM, CALIFORNIA CHART NO. 400

Figure 65

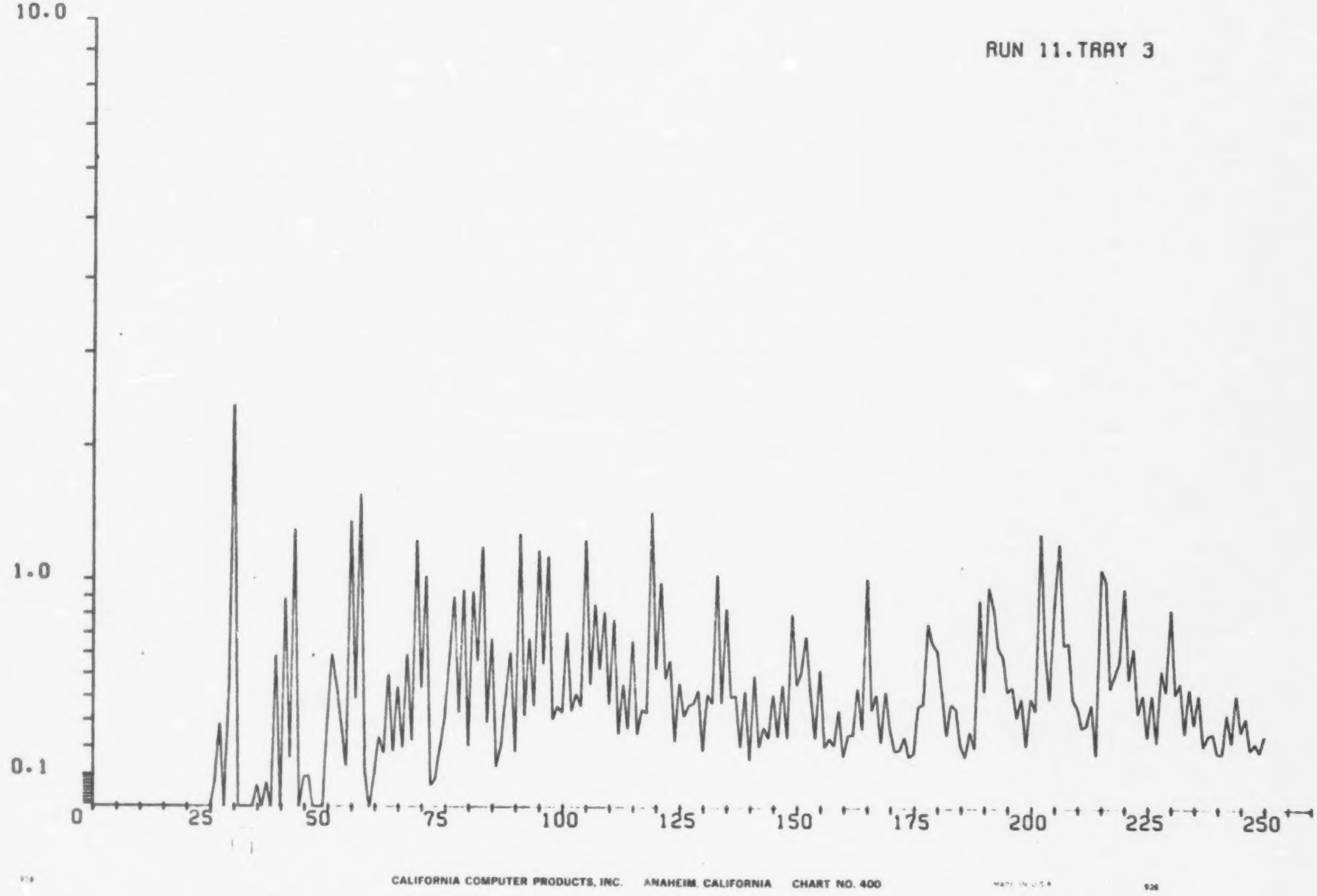

RUN 11.TRAY 3
10.0
1.0
0.1
0
25
50
75
100
125
150
175
200
225
250
CALIFORNIA COMPUTER PRODUCTS, INC. ANAHEIM, CALIFORNIA CHART NO. 400

Figure 66

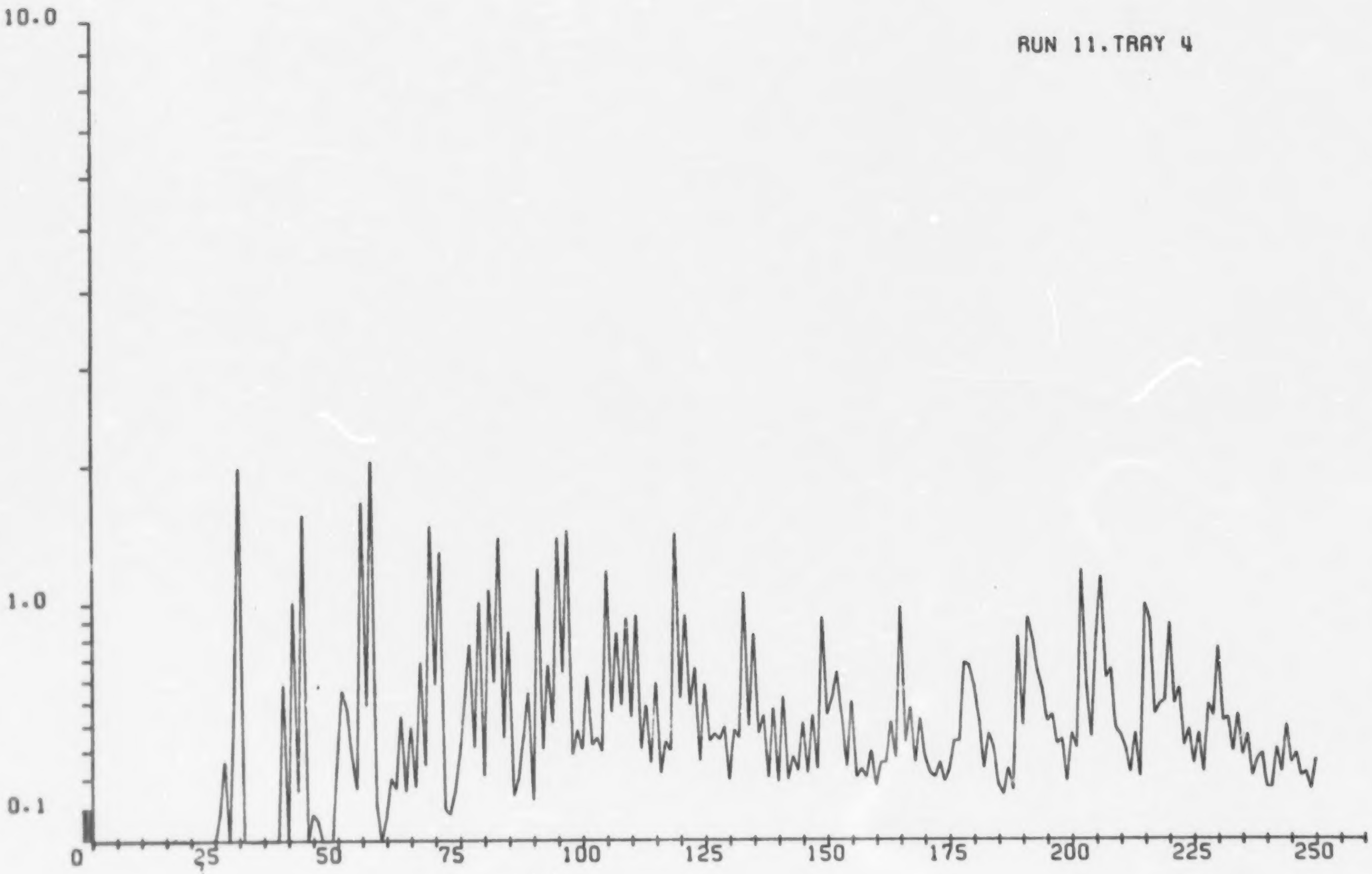
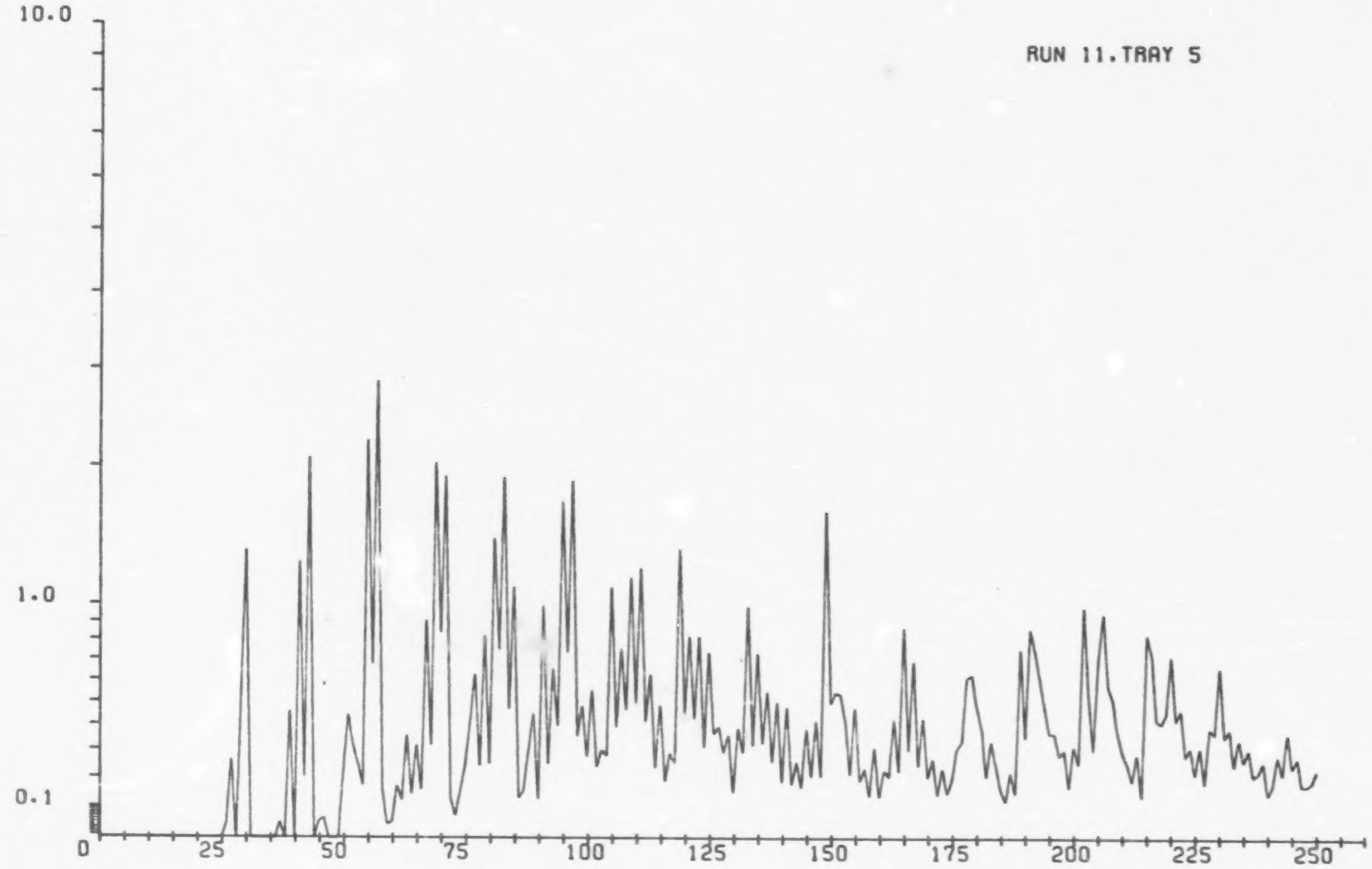


CHART NO. 400

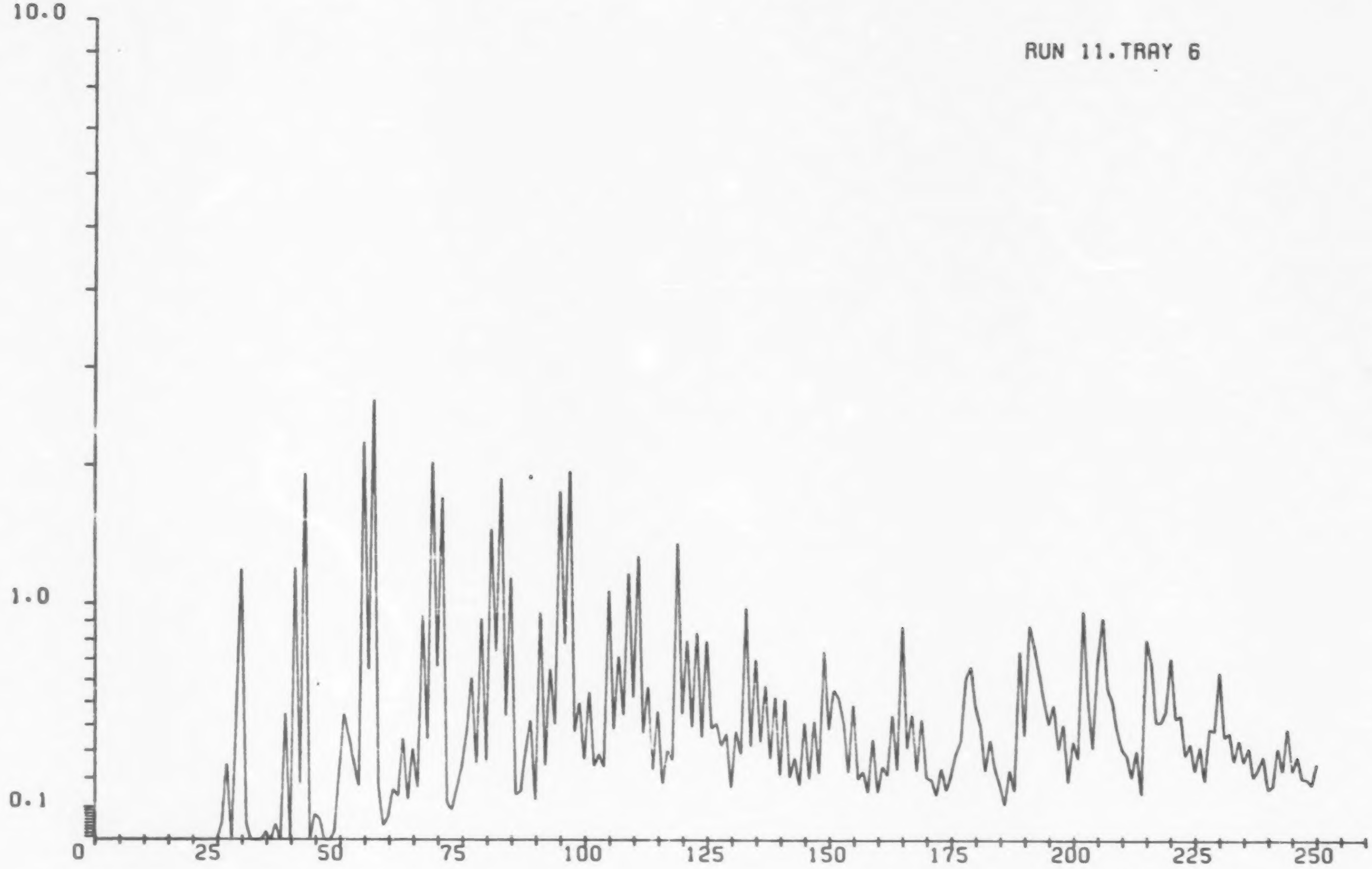
CALIFORNIA COMPUTER PRODUCTS, INC. ANAHEIM CALIFORNIA CHART NO. 400

Figure 67



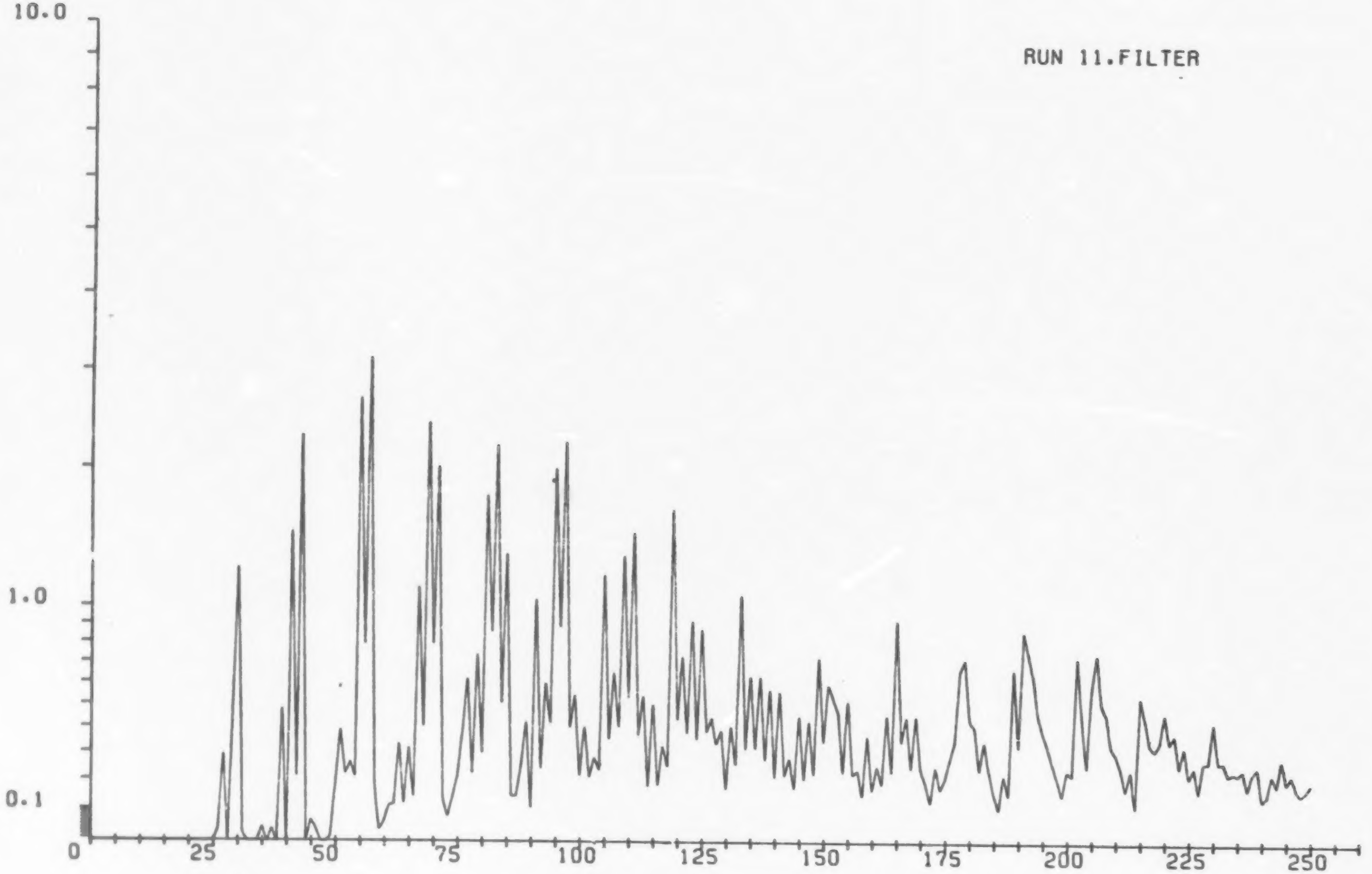
TER PRODUCTS INC ANAHEIM CALIFORNIA CHART NO. 400 CALIFORNIA COMPUTER PRODUCTS, INC

Figure 68



CALIFORNIA COMPUTER PRODUCTS, INC. ANAHEIM, CALIFORNIA CHART NO. 400

Figure 69



CALIFORNIA COMPUTER PRODUCTS, INC. ANAHEIM CALIFORNIA CHART NO. 400

Figure 70

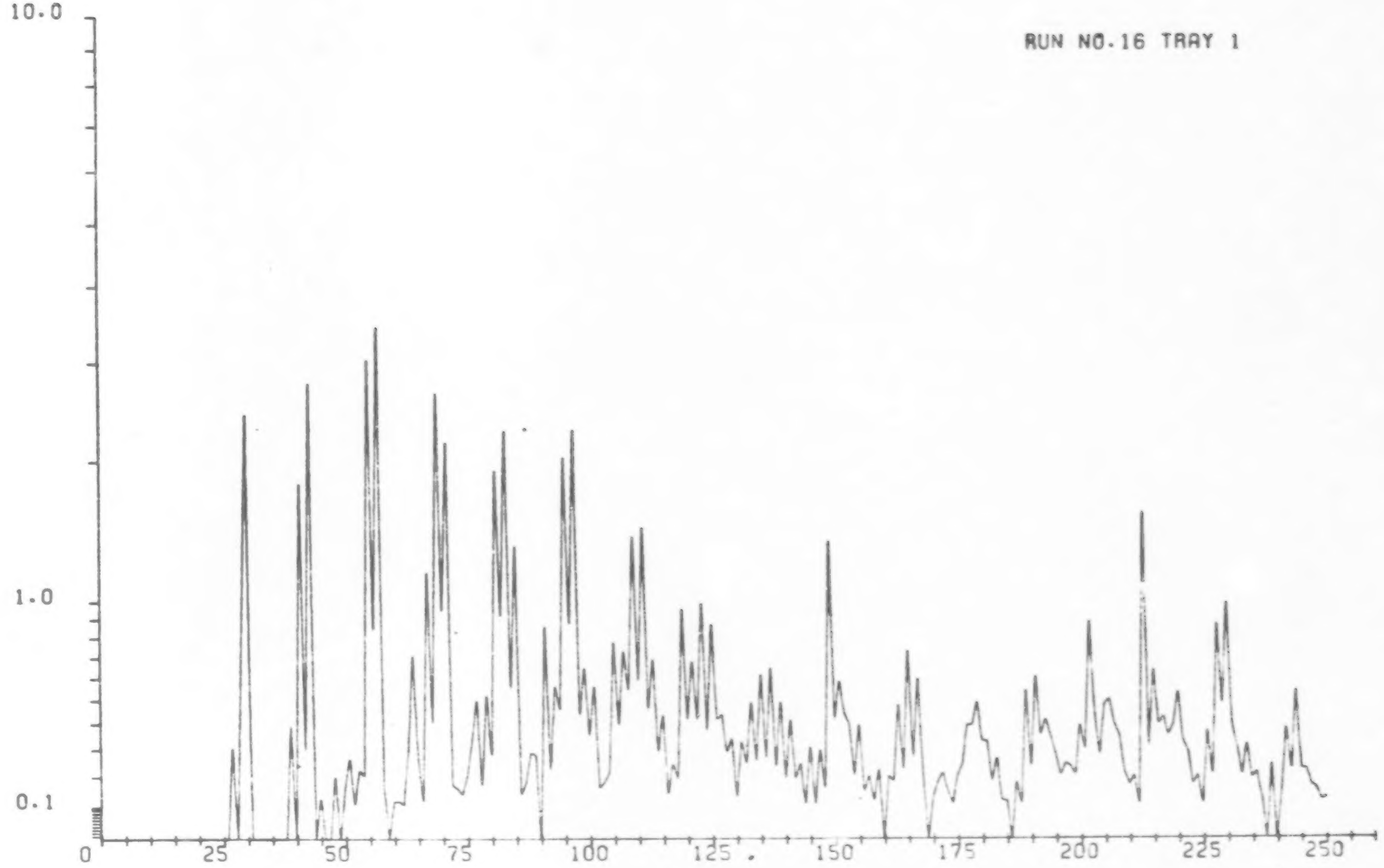


Figure 71

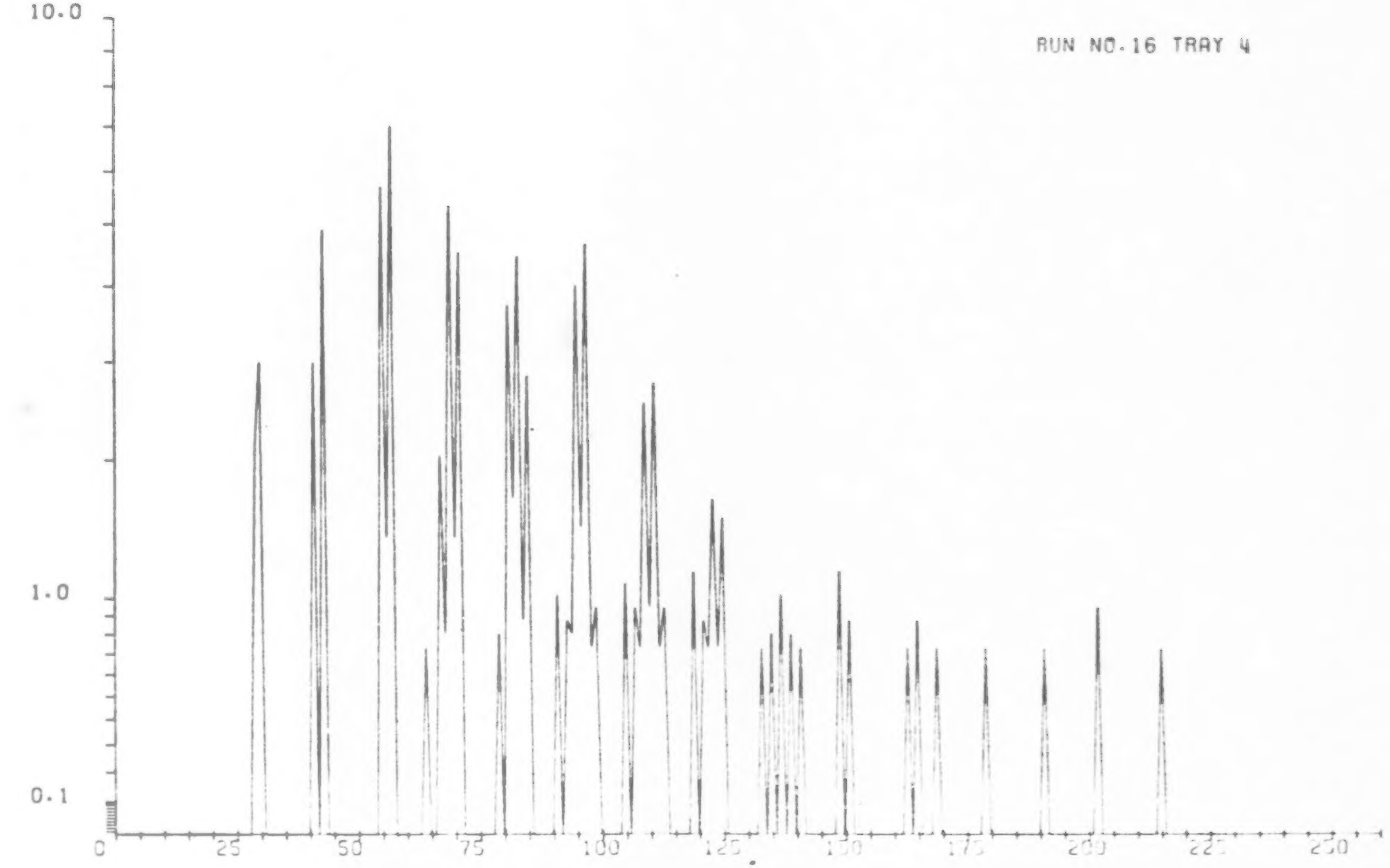


Figure 72

Table 18

RELATIVE VALUES OF THE AMOUNT OF NH_3, H_2O,
HCl, AND ORGANIC MATERIAL PRESENT IN ANDERSEN
AND FILTER SAMPLES BY MASS SPECTROMETRY

Run #	Plate	NH_3/ mg sample	H_2O/ mg sample	HCl/ mg sample	Organic Level/ mg sample	Sample Wt. (mg)
4	Slit A	0.0017	0.027	0	0.020	10.10
4	B	0.003	0.096	0	0.11	10.40
4	C	0.03	0.070	0	0.066	10.25
4	D	0.03	0.086	0	0.093	7.50
4	E	0.03	0.11	0	0.066	9.15
4	F	0.03	0.12	0	0.066	4.70
4	G	0.03	0.10	0.002	0.060	2.00
4	1	0.013	0.013	0.004	0.084	28.20
4	2	0.013	0.014	0.002	0.109	17.10
4	3	0.017	0.019	0.002	0.131	11.25
4	4	0.051	0.048	0.023	0.387	5.00
4	5	0.143	0.089	0.134	3.120	4.90
4	6	0.247	0.089	0.183	1.654	3.30
4	Filter	0.258	0.133	0.161	0.877	4.90

I. ULTRAVIOLET FLUORESCENCE SPECTRA - (R. A. Bredeweg)

Automobile exhaust particles were extracted with cyclohexane and the ultraviolet and fluorescence spectra were run. The absorbance at 255mμ and the fluorescence area using an exciting wavelength of 290mμ were used to calculate relative amounts of UV absorbing and fluorescent compounds present. The total amount of absorbing and fluorescent compounds do not seem to vary significantly from one run to the next, however, the amount present in a given sample weight increases with non-leaded gasoline and with the decreasing particle size.

1. Introduction

A quick standard procedure for the determination of relative amounts of aromatic organic materials present in automobile exhaust particles was needed. Since inadequate time was available to develop separation procedures and determine individual components, a general procedure of determining the ultraviolet absorbance and a value for fluorescence was used. These techniques detect the aromatic organics present including the poly-nuclear aromatics. Samples were received on Andersen glass plates and in bottles. The bottled samples had been obtained by sweeping out the inside of a tube used in place of the exhaust system and from trays that were located beneath slits in the tube.

2. Procedure

a. Sample Handling

The residue from the Andersen glass plates was scraped loose with a razor blade and transferred to a small tared watch glass with a small camel hair brush. The sample weight was obtained using a Mettler micro balance. The sample was then transferred to a 15 ml screw cap centrifuge tube (the cap of the tube should be lined with foil or Teflon) and 2-10 ml of cyclohexane (purified by passing through a silica column) was added depending on expected organic concentration.

Andersen plates with <1 mg of residue present were handled by placing the glass filter in a petri dish and adding 5 ml of the cyclohexane.* The dish was rotated in such a manner as to rinse the filter thoroughly, then the solution was transferred to a screw-cap centrifuge tube. The procedure was repeated with 5 more ml of solvent and the solution evaporated to 2 ml by passing a stream of nitrogen over the solution. The sample weight was obtained by weighing the filter before and after use.

---

*Run #5 - May have low results since an attempt was made to scrape the small amount of sample from the filter rather than washing it off with solvent.

Approximately 10 mg of the bottled samples were weighed in a small porcelain boat and transferred to the 15 ml screw-cap centrifuge tubes and 10 ml of solvent added.

The centrifuge tubes were capped tightly and the caps prevented from loosening by wrapping with rubber tape. The tubes were placed on their sides in an automatic shaker and shaken for a minimum of 5 hours. The rubber tape was removed and the solution centrifuged until clear and then the liquid was decanted into screw-cap bottles.

b. UV Absorption Measurements and Calculations

A Cary Model 15 spectrophotometer was used with 1-cm silica cells. When adequate solution was not available, a 1-cm semi-micro cell (volume ≈0.5 ml) was used. The solutions were scanned from 400-220mμ, diluting when necessary to keep the absorbance less than 2.0. All the samples gave very similar shaped spectra with a distinct maximum at 255mμ The absorbance at 255mμ was used as a measure of the organic content. A relative value of UV absorbing material present was obtained by calculating the absorbance for 1.0 mg of residue in 1.0 ml of solvent x 1000 (Tables 19 and 21). An estimation of the relative total absorbing material present on an Andersen plate can be obtained by multiplying the sample weight in mg times the number obtained above.

c. Fluorescence Measurements and Calculations

An Aminco-Bowman spectrophotofluorometer equipped with a Moseley model 135AMX-Y recorder and standard 1-cm cells, polished on all sides, was used for the fluorescence measurements. When adequate solution was not available, a semi-micro cell (Volume ~0.5 ml), polished on all sides, was used by placing the narrow portion facing the excitation

Table 19

RELATIVE AMOUNTS OF UV ABSORBING MATERIAL PRESENT ON ANDERSEN PLATES

Run #	Plate #2		Plate #4		Plate #5	
	mg sample	Absorbance*	mg sample	Absorbance*	mg sample	Absorbance*
3	7.93	240	2.19	750	1.40	2020
4	24.6	520	13.7	850	6.15	4620
4	10.8	560	6.27	680	3.54	1550
5	0.13	810	0.18	360		
6	8.56	680	2.71	2620	3.92	2940
7	15.3	720	8.73	830		
8	22.7	380	8.27	1000		
9	15.4	730	7.86	1810	4.93	4460
11	24.1	640	6.34	1780	5.39	4220
12	19.7	370	8.55	860	7.32	2360
13	14.9	500	5.34	1950	3.38	3440
14	8.49	300	4.44	480	2.65	1160
15 Blank	0.1	2400			<0.1	assuming 0.1 mg 13400
16	1.1	13500	0.3	34400	0.6	17500
17	0.9	8670	0.6	10700	1.0	6940

*Values are calculated on a basis of Absorbance @255mμ for 1.0 mg of sample in 1.0 ml of solvent x 1000. A relative value for the total amount UV absorbing material on a particular plate can be obtained by multiplying the sample weight in mg times the above value.

mg sample = Sample weight in milligrams

Table 20

RELATIVE AMOUNTS OF FLUORESCENT MATERIAL PRESENT ON ANDERSEN PLATES

Run #	Plate #2		Plate #4		Plate #5	
	mg sample	Fluorescence*	mg sample	Fluorescence*	mg sample	Fluorescence*
3	7.93	240	2.19	570	1.40	1580
4	24.6	190	13.7	440	6.15	1790
4	10.8	240	6.27	350	3.54	880
5	0.13	840	0.18	500		
6	8.56	260	2.71	1320	3.92	1750
7	15.3	310	8.73	470		
8	22.7	130	8.27	420		
9	15.4	140	7.86	280	4.93	320
11	24.1	60	6.34	250	5.39	190
12	19.7	70	8.55	180	7.32	190
13	14.9	110	5.34	320	3.38	550
14	8.49	100	4.44	230	2.65	180
15 Blank	0.1	650			<0.1	assuming 0.1 mg 5400
16	1.1	290	0.3	3570	0.6	2260
17	0.9	1480	0.6	2380	1.0	1480

---

*Values are calculated on the basis of area (in.^{2} x 100, with a planimeter) for 1.0 mg of sample in 1.0 ml of solvent, with instrument settings of excitation wavelength = 290mμ, slits = 2mm, sensitivity = 0.01, and vertical scale of recorder at a setting of 5. A relative value for the total amount of fluorescent material on a particular plate can be obtained by multiplying the sample weight in mg times the above value.

Table 21

RELATIVE AMOUNTS OF UV ABSORBING AND FLUORESCENT MATERIALS PRESENT IN SWEEPING AND SLIT SAMPLES

(See Notes at Bottom of Tables 19 and 20)

Run #		Sample Wt. in mg	Relative Absorbance Values	Relative Fluorescent Values
13 - Sweeping	A	9.49	340	320
	B	9.41	180	110
	C	9.31	180	110
	D	8.95	600	300
	E	8.85	800	350
	F	7.69	910	340
	G	12.1	770	290
Slit	1	11.1	40	20
	2	7.90	50	30
	3	9.49	20	20
14 - Sweeping	A	13.4	210	160
	B	9.83	90	50
	C	11.9	40	30
	D	8.70	270	140
	E	4.48	1010	510
Slit	1	8.87	50	30
	2	10.0	30	10

source and the wide portion (1 cm of solution) facing the detector. Various excitation wavelengths were examined (290, 330, and 353mμ) with 290mμ giving, in general, the most detailed and intense spectra. Exceptions to this are plate #5 from runs 9, 11, 12, 13, 14, and 16 and all of run 17, where the 353mμ exciting wavelength gives a more intense spectra (353mμ is used by some authors for determining polynuclear aromatic compounds). The area in in.^{2} x 100 under the fluorescence peaks at an excitation wavelength of 290mμ was determined with a planimeter. A relative value of the fluorescence area for 1.0 mg of residue in 1.0 ml of solvent at a sensitivity setting of 0.01, with all slits at 2mm, the wavelength (x) scale on the recorder set at 20 fixed and the intensity (y) scale on the recorder set at 5 fixed (Tables 20 and 21). An estimation of the relative total fluorescent material present on an Andersen plate can be obtained by multiplying the sample weight in mg times the number obtained above.

3. Discussion of Results

The absorbance and fluorescence values tend to give similar variations on all the samples. In general, the smaller particles have the highest concentration of detectable organic material present. The concentration also increases when no additive gasolines are used; however, the total residue is also decreasing and, therefore, the total detectable organics in a given size range do not vary significantly with additive. The sweeping samples indicate an increase in organics at a further distance down the tube, while the slit samples are very low, which may be due to the low contact with exhaust fumes. The fluorescence curves may be the most useful in the future in correlating to actual percentage amounts of various classes of organic compounds, since spectra has been obtained at excitation wavelengths of 290, 330, and 353mμ.

J. PARTICLE TRACE METAL ANALYSIS

Trace metal analysis of particulate samples from all sources has been conducted for run #11 and #12 (Indolene HO 30 steady-state and cycled). Analysis is by Emission Spectroscopy and the data is presented in Table 22.

Table 22

PARTICULATES: TRACE METAL ANALYSIS

Run #11	Slit Samples		Sweeping Samples						
Wt. %	1	2	A	B	C	D	E	F	G
Fe	4.0	5.6	3.9	6.0	5.8	3.8	3.2	2.1	2.2
Cu	0.012	0.015	0.009	0.011	0.011	0.012	0.008	0.008	0.010
Al	0.092	0.16	0.044	0.065	0.056	0.064	0.050	0.042	0.069
Ca	0.071	0.065	0.059	0.058	0.073	0.079	0.10	0.084	0.13
Si	0.060	0.13	0.062	0.036	0.057	0.038	0.046	0.047	0.085
Mg	1.8	1.3	0.63	1.1	1.0	0.86	0.58	0.55	0.54
Mn	0.035	0.044	0.026	0.043	0.039	0.032	0.026	0.018	0.022
Cr	0.042	0.043	0.024	0.031	0.029	0.028	0.022	0.021	0.026
Sn	0.033	0.024	0.012	0.019	0.016	0.015	0.011	0.010	0.010
Zn	3.8	6.1	3.0	4.6	4.5	1.0	0.47	0.39	0.52
Ti	<0.010	<0.010	<0.010	<0.010	0.011	0.013	0.016	0.017	0.020
Ni	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Mo	0.011	0.007	0.005	0.009	0.008	0.007	0.005	0.005	0.006

	Andersen Tray						
Wt. %	1	2	3	4	5	6	Filter
Fe	.16	.19	.15	.24	.18	.15	.098
Cu	.018	.026	.034	.040	.034	.054	.008
Al	.032	.08	.048	.11	.11	.12	.023
Ca	.13	.10	.18	.30	.36	.23	.095
Si	.039	.038	.036	.068	.05	.038	<.01
Mg	.066	.063	.11	.32	.43	.16	.005
Mn	<.005	.005	<.01	<.01	<.01	<.01	<.005
Cr	<.01	.012	<.025	<.025	<.025	<.025	<.01
Sn	<.01	<.01	<.025	<.025	<.025	<.025	<.01
Zn	.068	.059	.09	.14	.14	.11	.09
Ti	<.01	<.01	<.025	<.025	<.025	<.025	<.01
Ni	<.01	<.01	<.025	<.025	<.025	<.025	<.01

Run #12	Slit Samples		Sweeping Samples						
Wt. %	1	2	A	B	C	D	E	F	G
Fe	3.5	4.3	3.0	4.9	3.1	2.5	1.6	0.95	1.3
Cu	0.010	0.011	0.010	0.011	0.019	0.016	0.009	0.008	0.010
Al	0.080	0.062	0.055	0.075	0.076	0.13	0.063	0.064	0.043
Ca	0.031	0.063	0.025	0.032	0.036	0.088	0.078	0.050	0.12
Si	0.046	0.060	0.039	0.087	0.095	0.084	0.13	0.054	0.079
Mg	0.71	0.15	0.33	0.57	0.48	0.65	0.46	0.33	0.38
Mn	0.074	0.060	0.036	0.067	0.036	0.10	0.015	0.011	0.012
Cr	0.075	0.059	0.054	0.085	0.056	0.13	0.043	0.030	0.034
Sn	0.019	0.017	0.010	0.015	0.012	0.016	<0.010	<0.010	<0.010
Zn	4.4	9.3	5.4	7.0	9.7	4.2	0.51	0.32	0.41
Ti	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Ni	0.017	0.012	0.011	0.014	0.011	0.029	<0.010	<0.010	<0.010
Mo	0.010	0.007	0.007	0.008	0.005	0.008	0.006	0.004	0.005

	Andersen Plate						
Wt. %	1	2	3	4	5	6	Filter
Fe	.16	.14	.31	.39	.15	.16	.18
Cu	.038	.025	.032	.027	.027	.028	.006
Al	.074	.027	.044	.043	.072	.11	.010
Ca	.17	.17	.15	.29	.27	.29	.058
Si	.061	.03	.034	<.025	.072	.046	<.01
Mg	.086	.083	.073	.14	.22	.20	.027
Mn	<.005	<.005	<.005	<.01	<.01	<.01	<.005
Cr	<.01	<.01	<.01	<.025	<.025	<.025	<.01
Sn	<.01	<.01	<.01	<.025	.027	<.025	<.01
Zn	.069	.051	.061	.11	.11	.088	.069
Ti	<.01	<.01	<.01	<.025	.70	<.025	<.01
Ni	<.01	<.01	<.01	<.025	<.025	<.025	<.01

K. PARTICLE EMISSIONS

Emitted particulates, as noted earlier in this report, have been collected as four samples: i.e., tube sweepings, tube slit trays, Andersen samplers, and a "final" filter following the Andersen. This technique has allowed the capture and evaluation of essentially all particles emitted from the exhaust pipe. In general, particle sizes associated with these samples are:

tube - sweepings } >1000 to 20μ
slits

Andersen - 20μ to 0.5μ

filter - less than 0.5μ

The mass percentage distribution of emitted particles as related to these sources is shown in Figure 90 for all test fuels. Note in all cases that the tube sample, which includes sweepings and slit samples, is small compared to the Andersen and filter sources. Note also that the filter sample is, generally, the largest. Figure 91 provides a little different perspective to the data. It shows the grams/hour particles emitted as a function of the sample source for all test fuels. Total particle emissions are also indicated by a T above the bars representing each test fuel.

These data can best be understood by plotting cumulative particle size distribution curves. Such cumulative distribution data are represented by log-normal plots of stage D_{50} values (equivalent diameters for unit density spheres at 50% mass collection efficiency) against mass cumulative percent. Such plots for all test fuels are presented in Figures 73 through 78. D_{50} values for the Andersen samplers are as follows:

Andersen Stage	D_{50}-μ
1	9.0
2	5.35
3	2.95
4	1.53
5	0.95
6	0.54

Similar distribution curves for percent total Pb, Cl, Br, and organic are presented in Figures 79 through 89. Chlorine and bromine are determined by Neutron Activation Analysis of samples washed in a 1:1 ethanol:water solution. The sample is then digested in nitric acid and analyzed for lead by atomic absorption. Filter samples are analyzed by the same method except for lead which is determined gravimetrically as lead sulfate. However, complete analyses of the percentages of these materials in tube

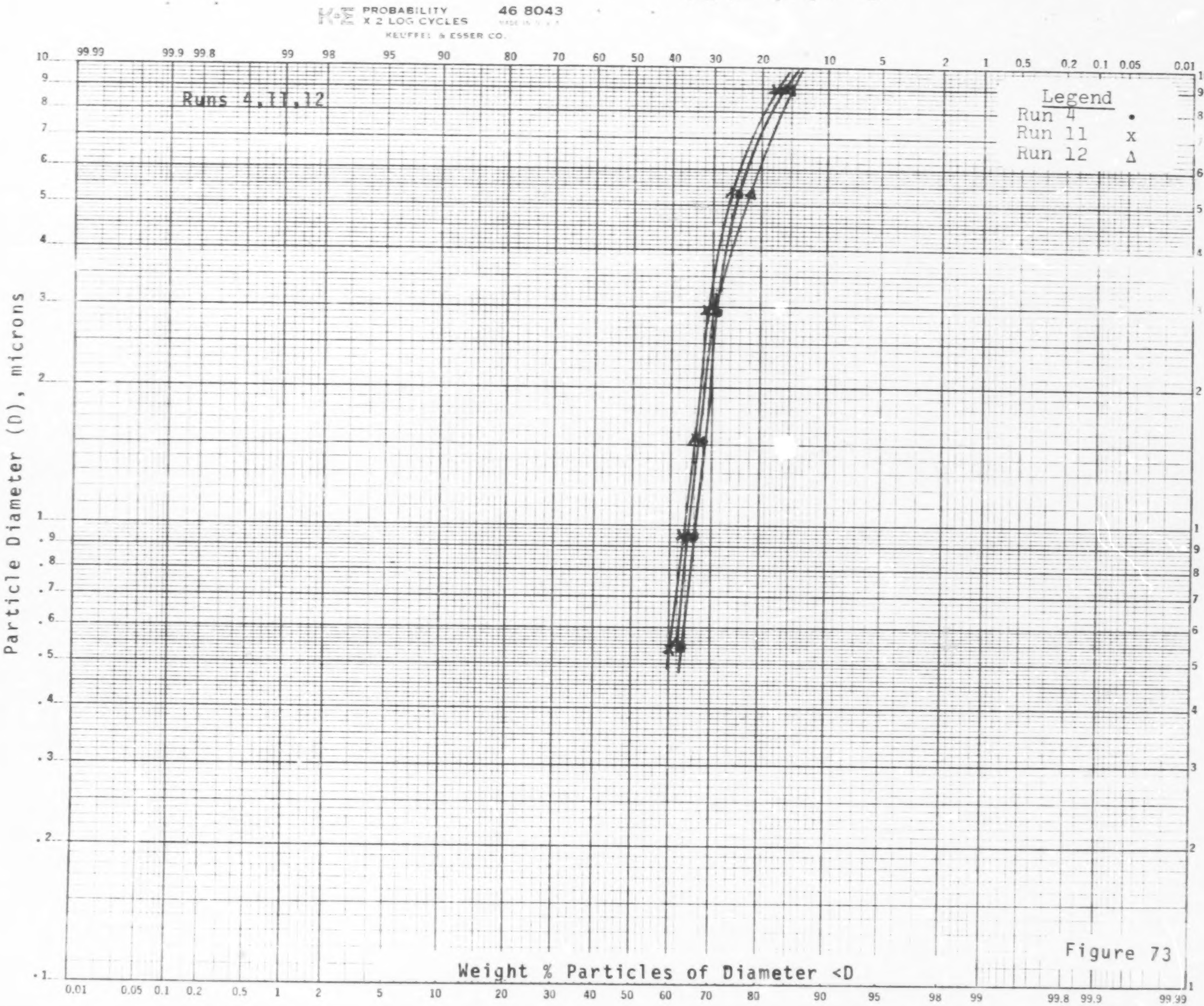

K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
Runs 4,11,12
Legend
Run 4 •
Run 11 x
Run 12 Δ
Particle Diameter (D), microns
Weight % Particles of Diameter <D
99.99 99.9 99.8 99 98 95 90 80 70 60 50 40 30 20 10 5 2 1 0.5 0.2 0.1 0.05 0.01
0.01 0.05 0.1 0.2 0.5 1 2 5 10 20 30 40 50 60 70 80 90 95 98 99 99.8 99.9 99.99
10 9 8 7 6 5 4 3 2 1 .9 .8 .7 .6 .5 .4 .3 .2 .1

Figure 73

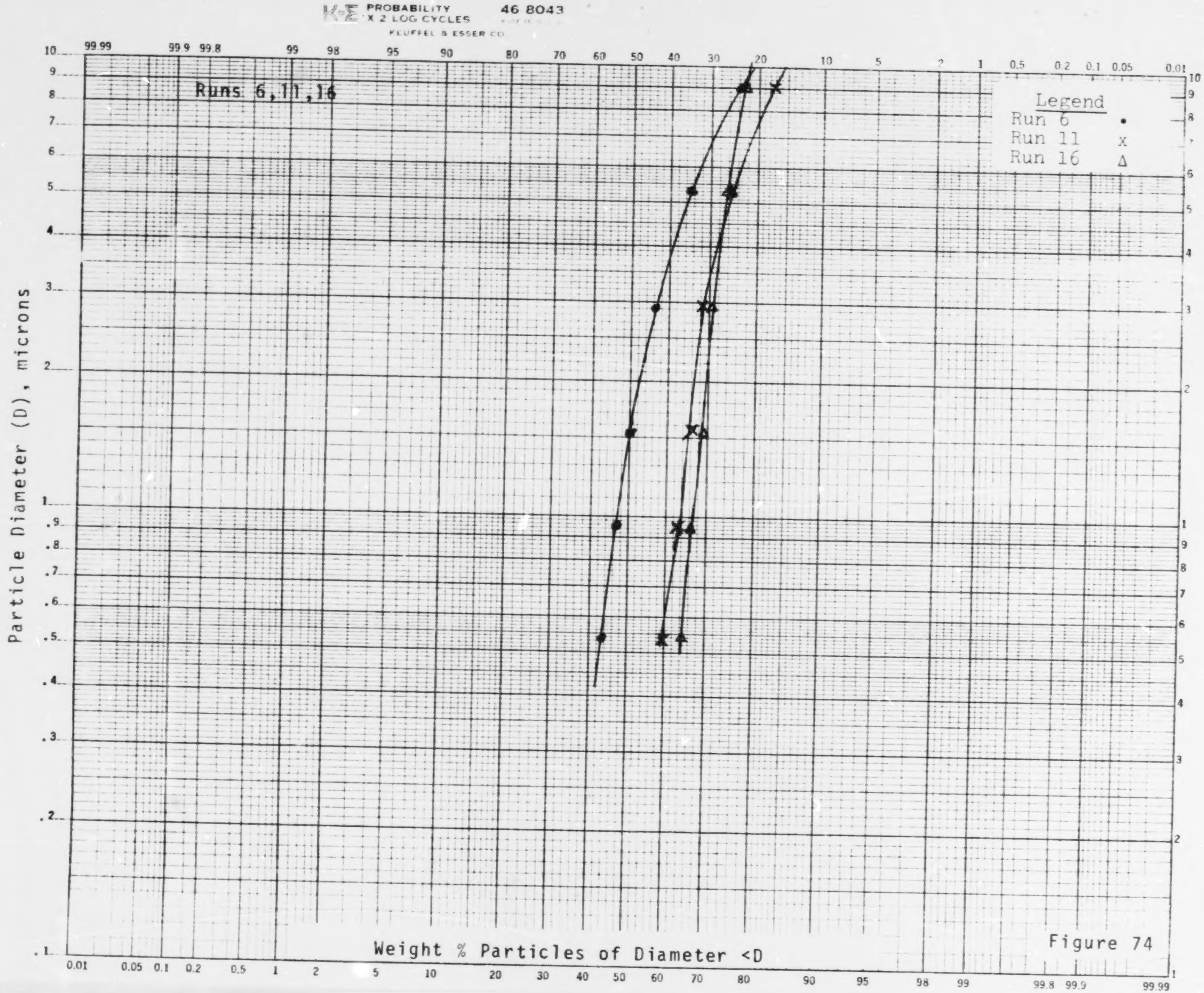


Figure 74

K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
Runs 6,11,16
Legend
Run 6 •
Run 11 x
Run 16 Δ
Particle Diameter (D), microns
Weight % Particles of Diameter <D
.1
.2
.3
.4
.5
.6
.7
.8
.9
1
2
3
4
5
6
7
8
9
10
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

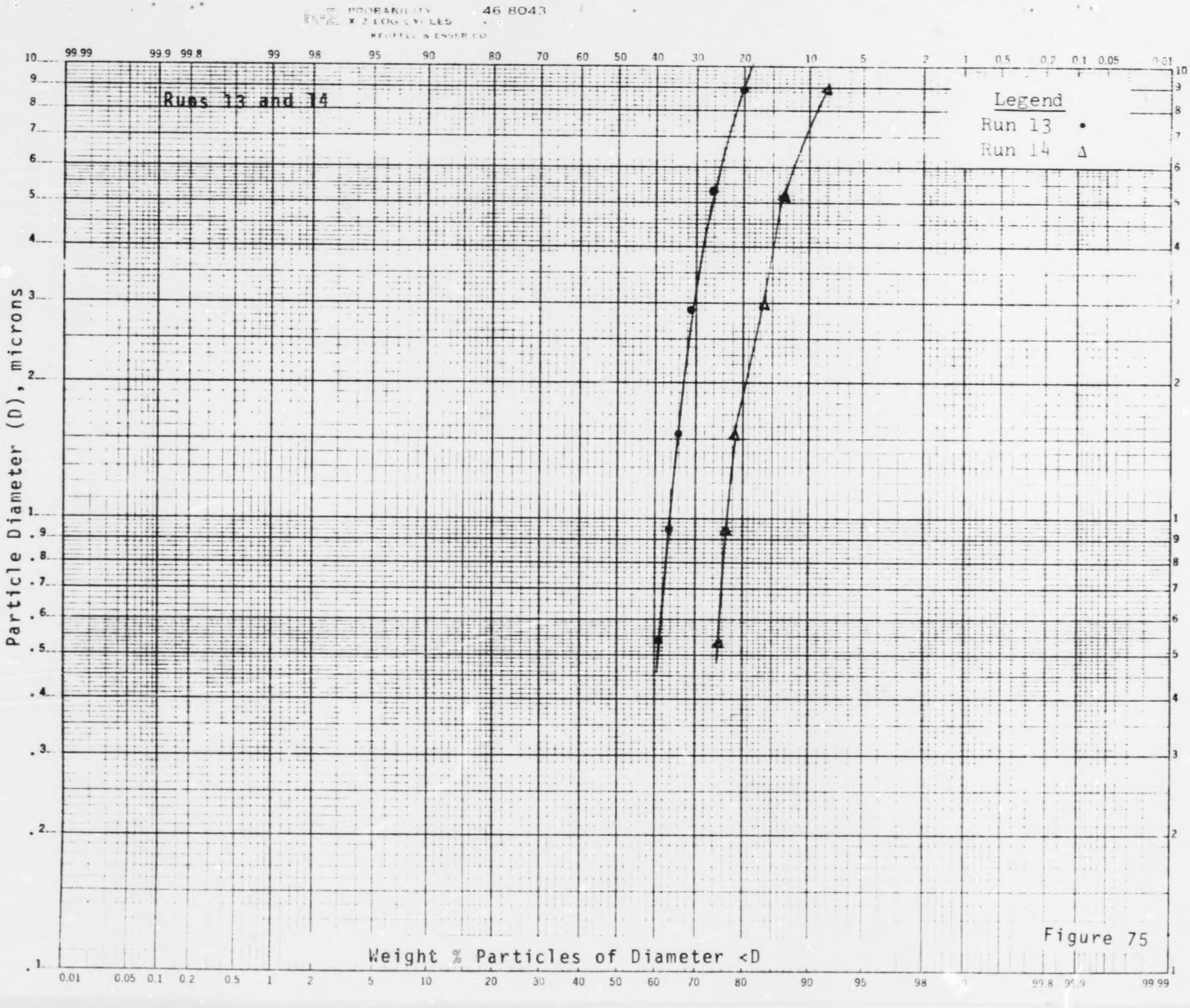

PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
Runs 13 and 14
Legend
Run 13 •
Run 14 Δ
Particle Diameter (D), microns
Weight % Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1

Figure 75

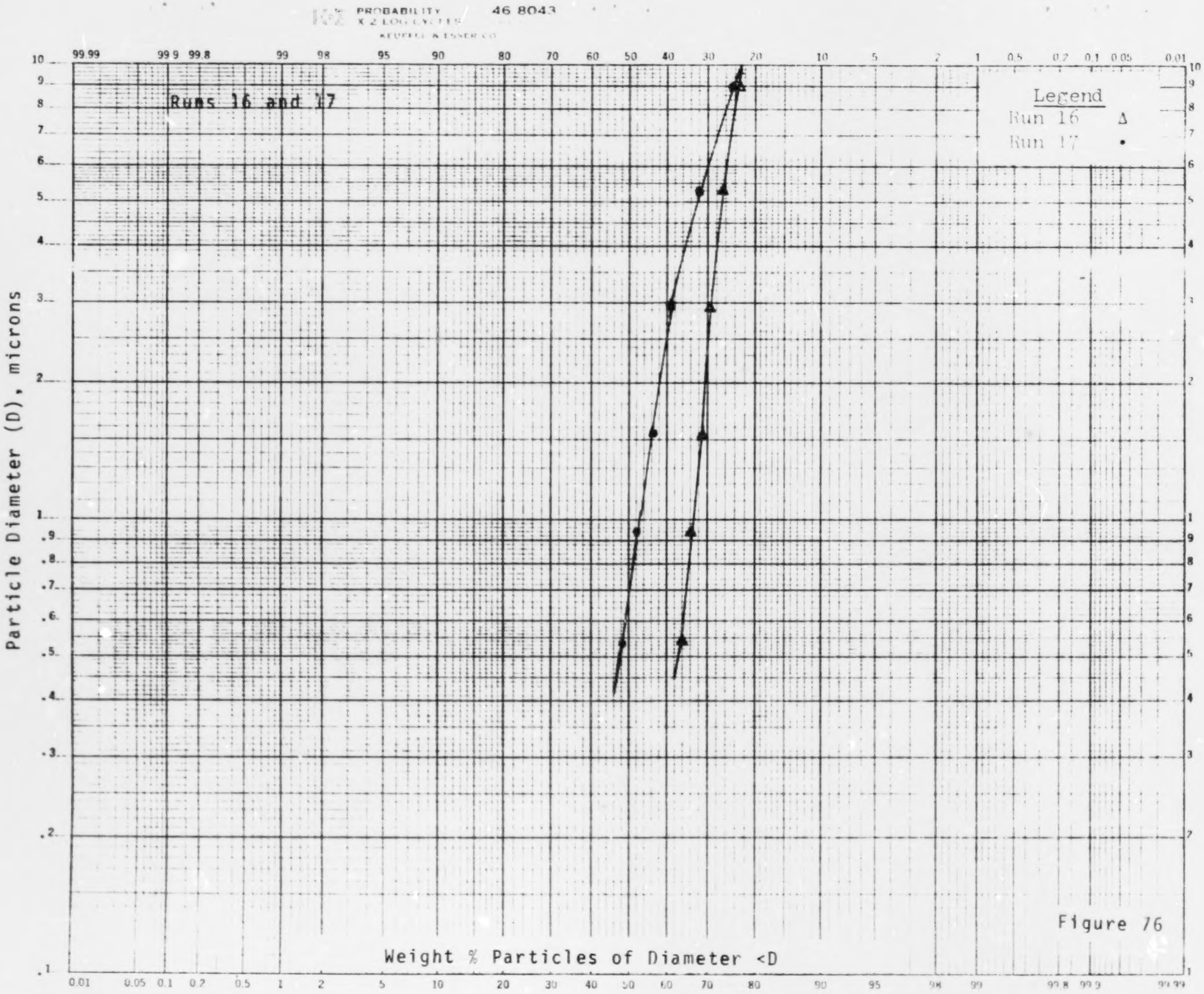

PROBABILITY X 2 LOG CYCLES
KEUFFEL & ESSER CO.
46 8043
Runs 16 and 17
Legend
Run 16 Δ
Run 17 •
Particle Diameter (D), microns
Weight % Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1

Figure 76

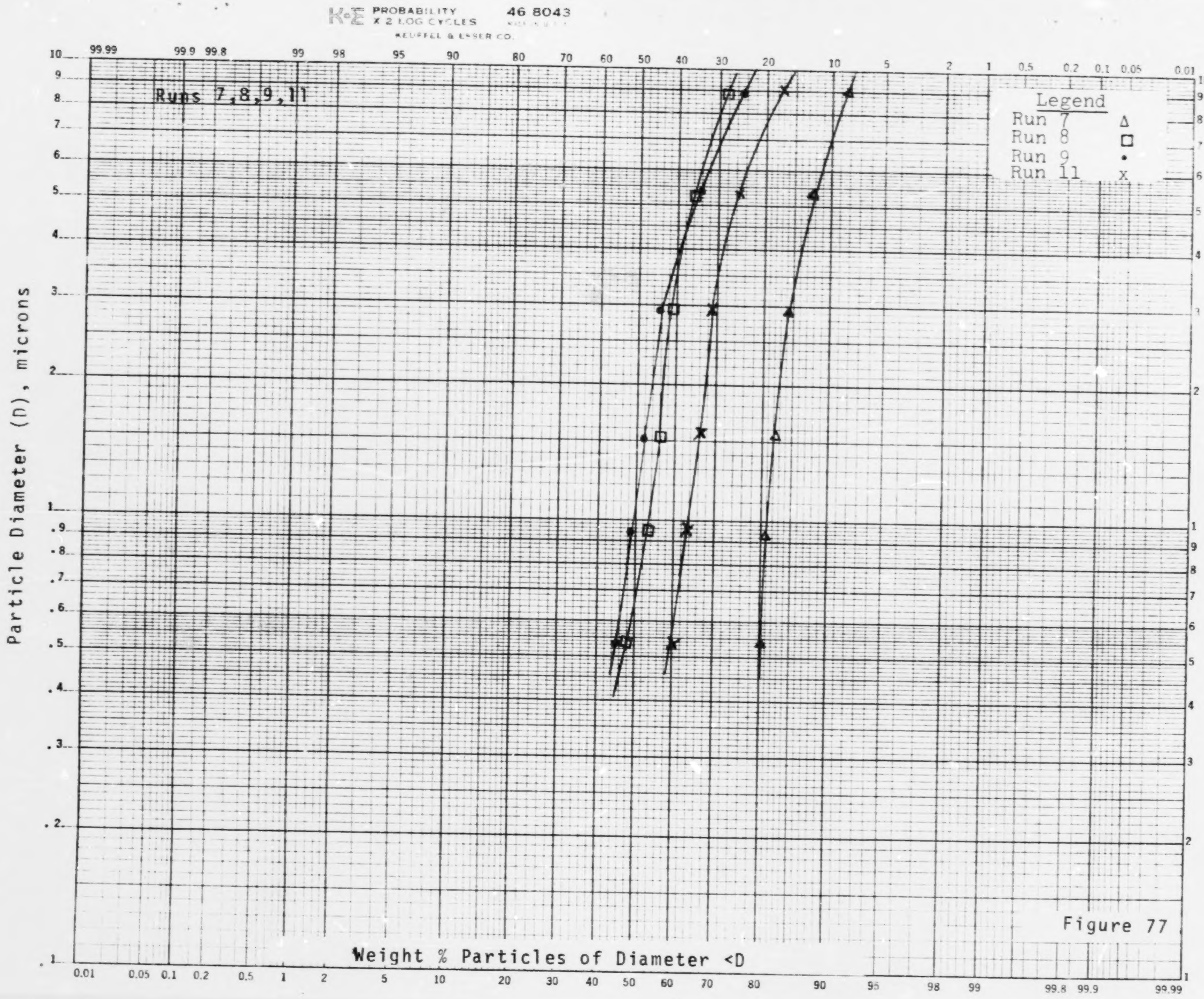

K&E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
Runs 7,8,9,11
Legend
Run 7 Δ
Run 8 □
Run 9 •
Run 11 x
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01 0.05 0.1 0.2 0.5 1 2 5 10 20 30 40 50 60 70 80 90 95 98 99 99.8 99.9 99.99
99.99 99.9 99.8 99 98 95 90 80 70 60 50 40 30 20 10 5 2 1 0.5 0.2 0.1 0.05 0.01
10 9 8 7 6 5 4 3 2 1 .9 .8 .7 .6 .5 .4 .3 .2 .1

Figure 77

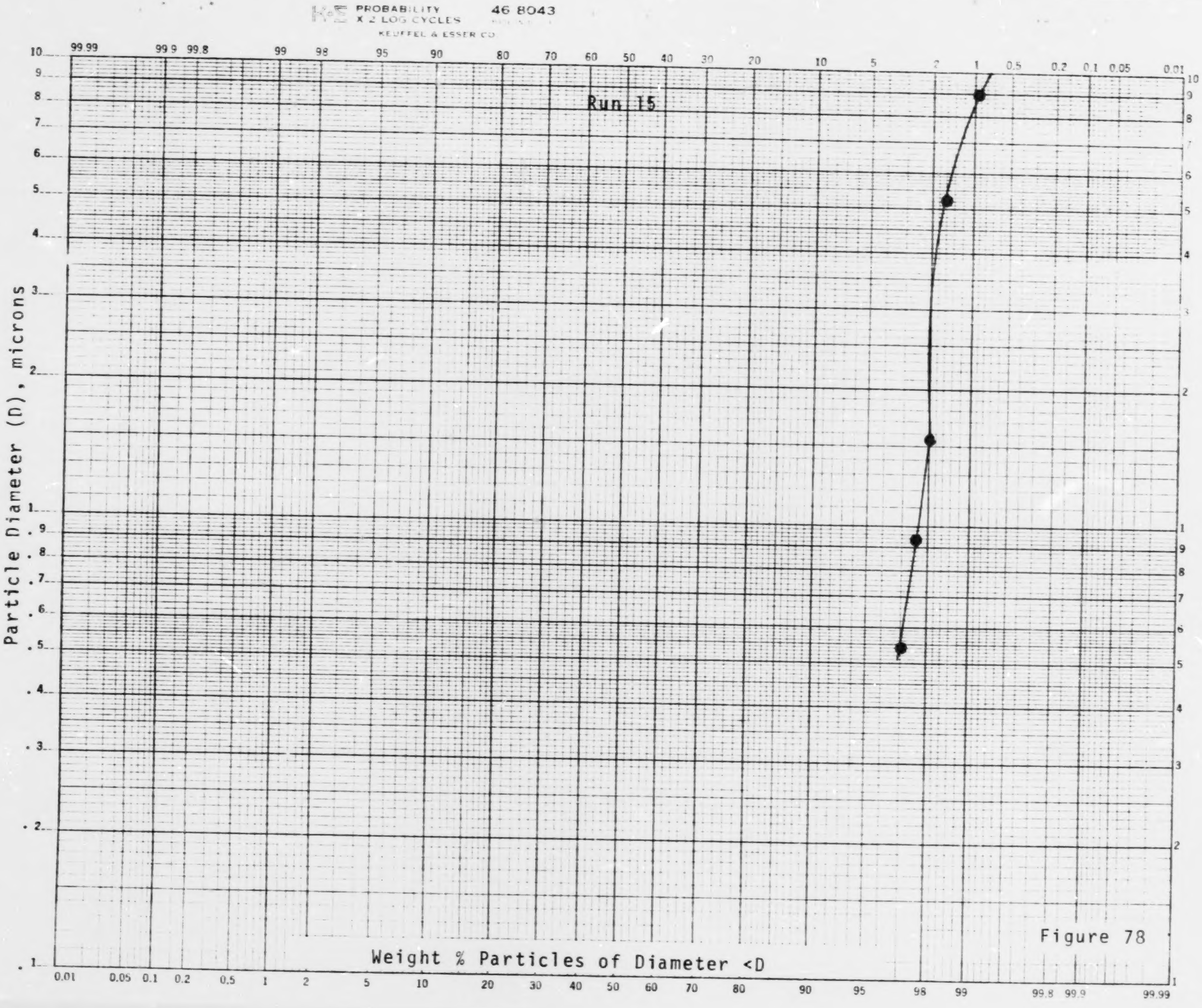

K&E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO
Run 15
Particle Diameter (D), microns
Weight % Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

Figure 78

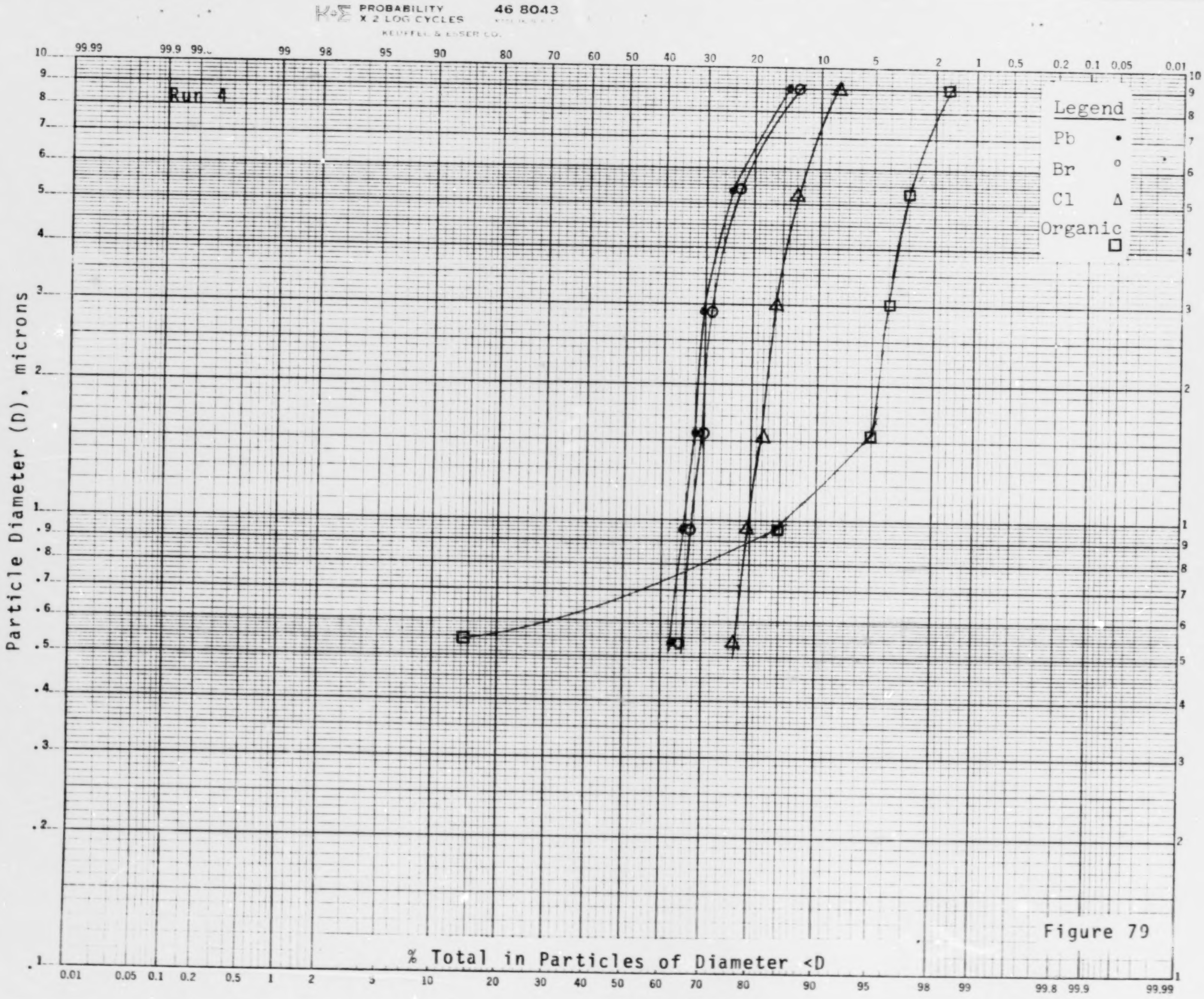

K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
Run 4
Legend
Pb •
Br ○
Cl Δ
Organic □
Particle Diameter (D), microns
% Total in Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
.1
.2
.3
.4
.5
.6
.7
.8
.9
1
2
3
4
5
6
7
8
9
10

Figure 79

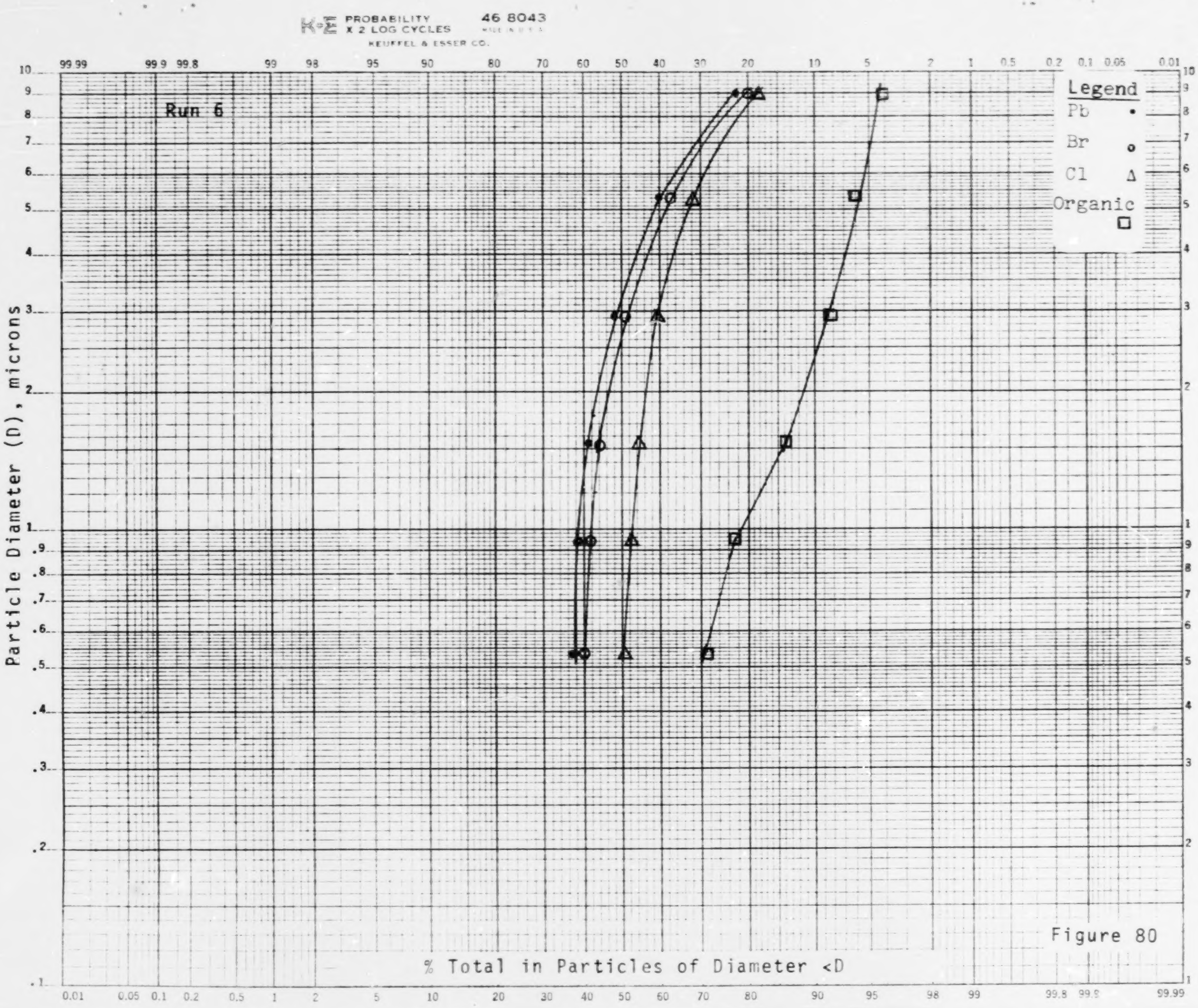


Figure 80
K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
Run 6
Legend
Pb •
Br o
Cl Δ
Organic □
Particle Diameter (D), microns
% Total in Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

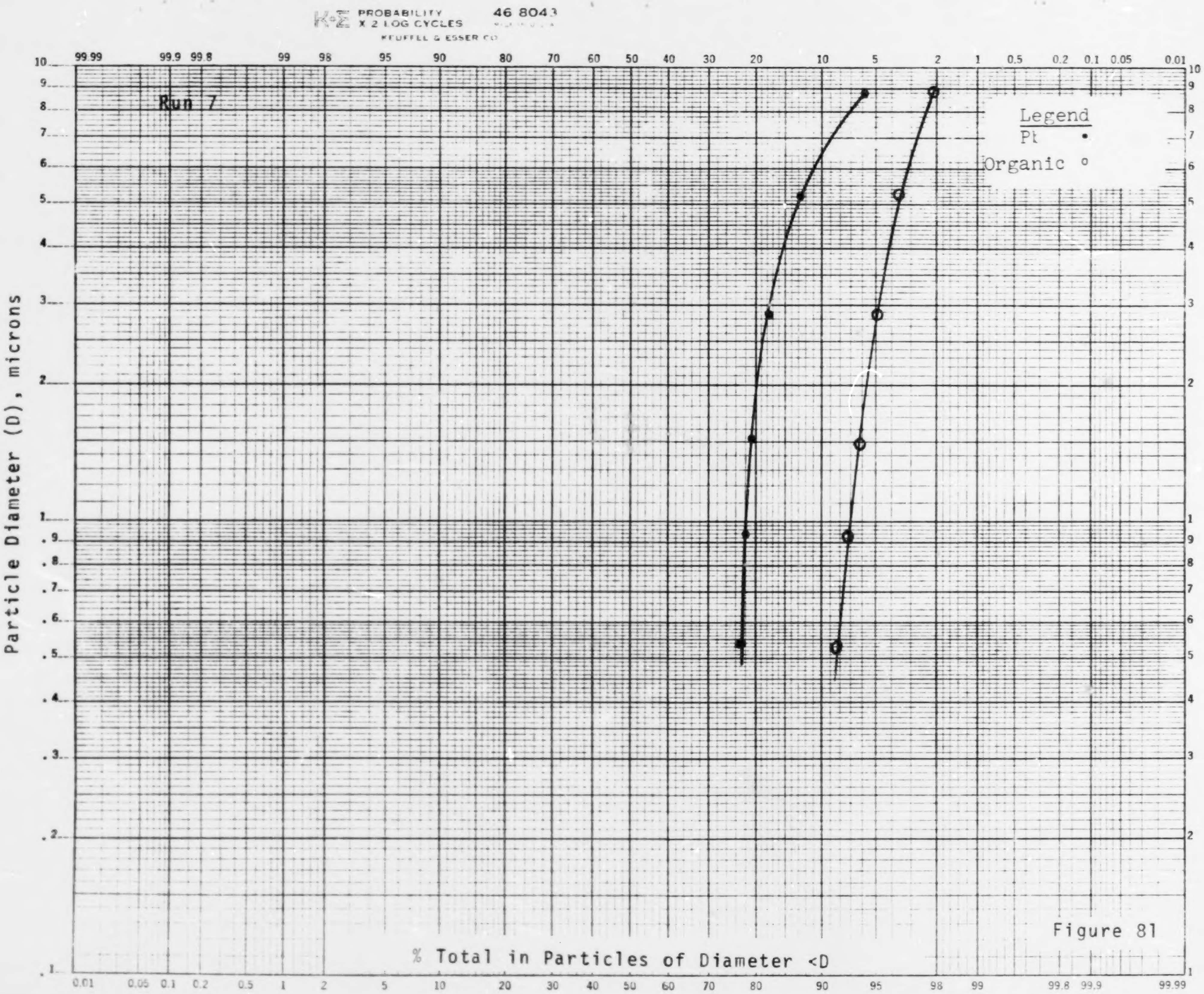

K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
Run 7
Legend
Pt •
Organic o
Particle Diameter (D), microns
% Total in Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1

Figure 81

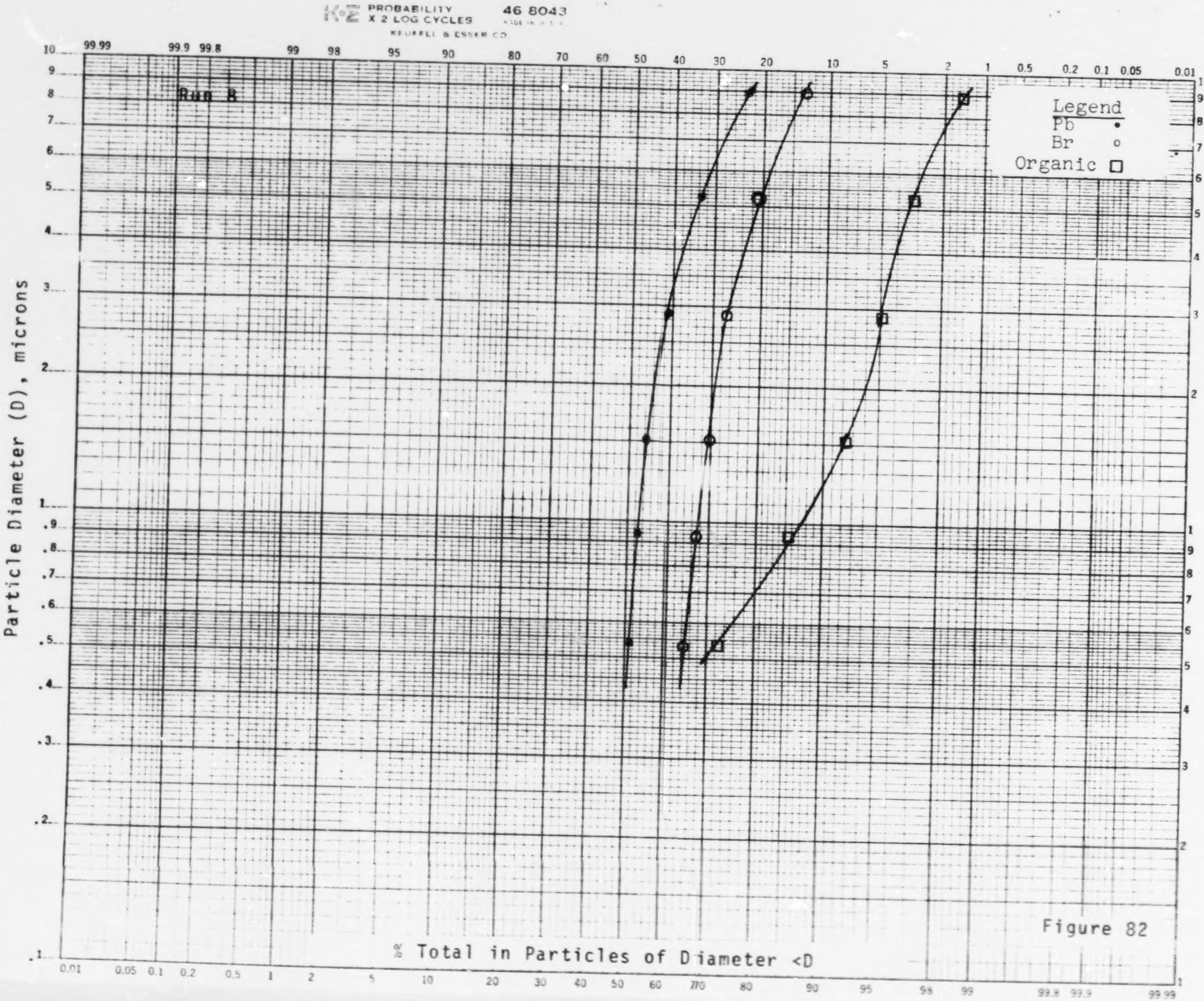

K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
Run 8
Legend
Pb •
Br ○
Organic □
Particle Diameter (D), microns
% Total in Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

Figure 82

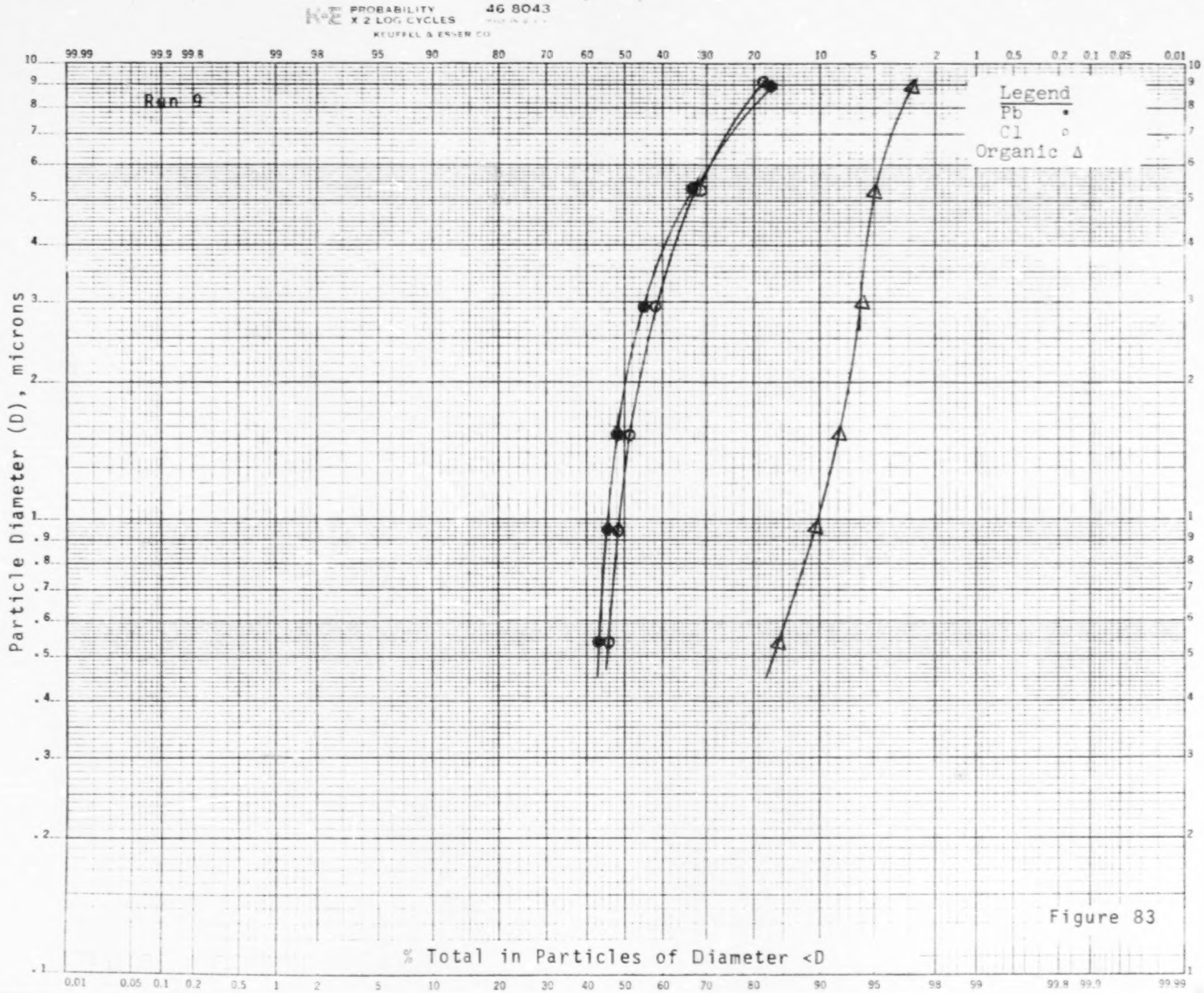

K&E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
Run 9
Legend
Pb •
Cl ○
Organic Δ
Particle Diameter (D), microns
% Total in Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

Figure 83

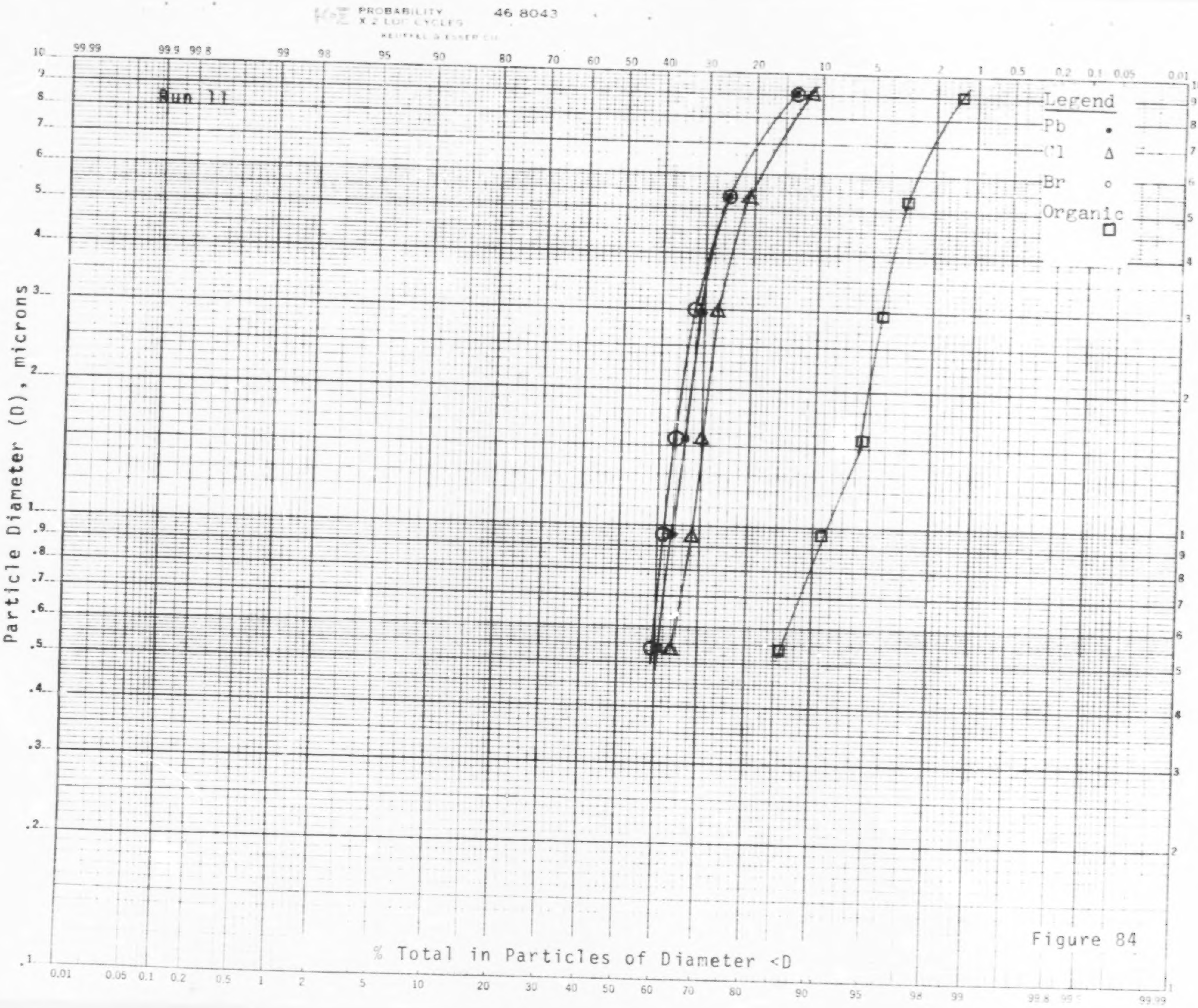

K&E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
Run 11
Legend
Pb •
Cl Δ
Br ○
Organic □
Particle Diameter (D), microns
% Total in Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1

Figure 84

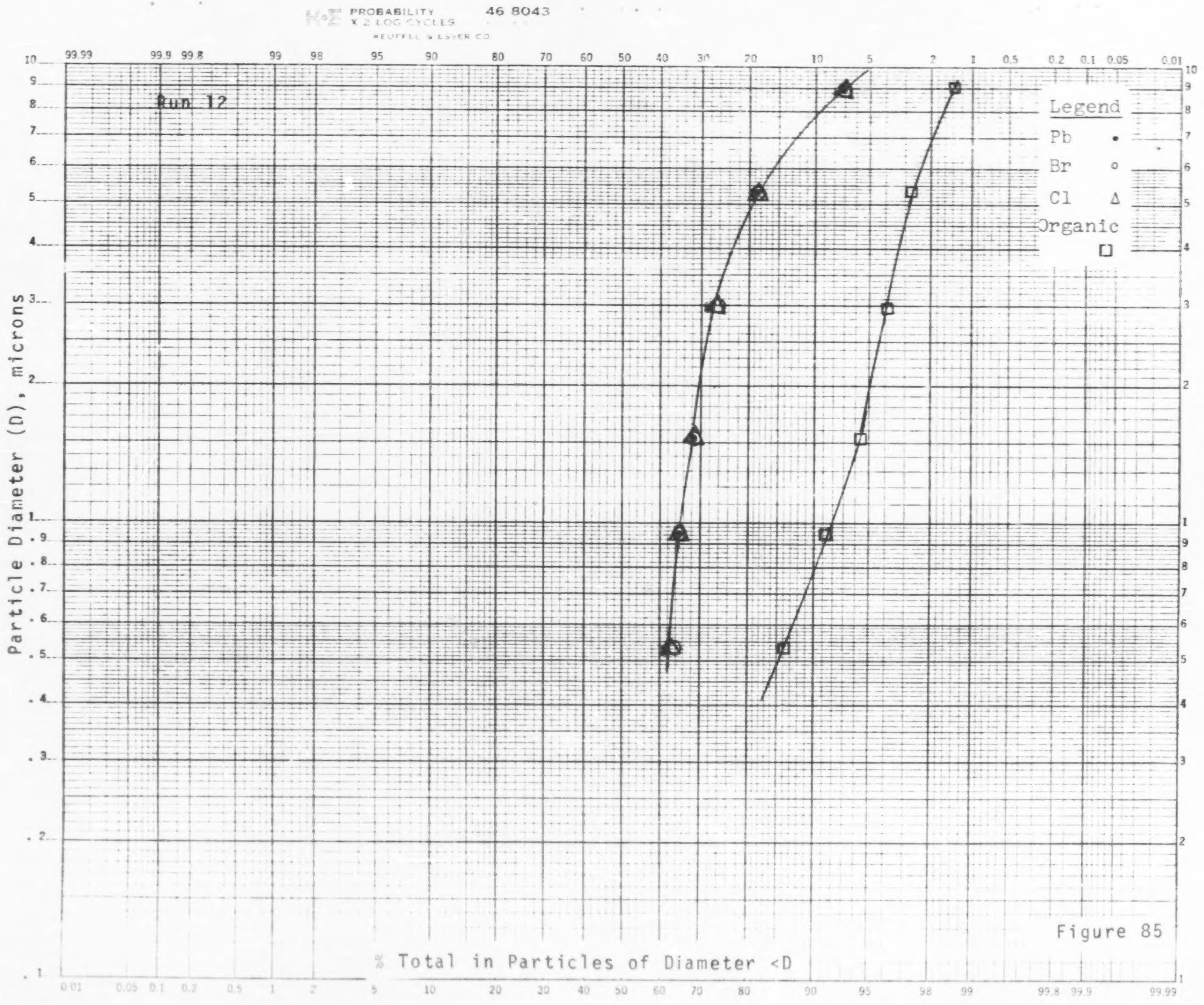

K&E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
Run 12
Legend
Pb •
Br o
Cl Δ
Organic □
Particle Diameter (D), microns
% Total in Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1

Figure 85

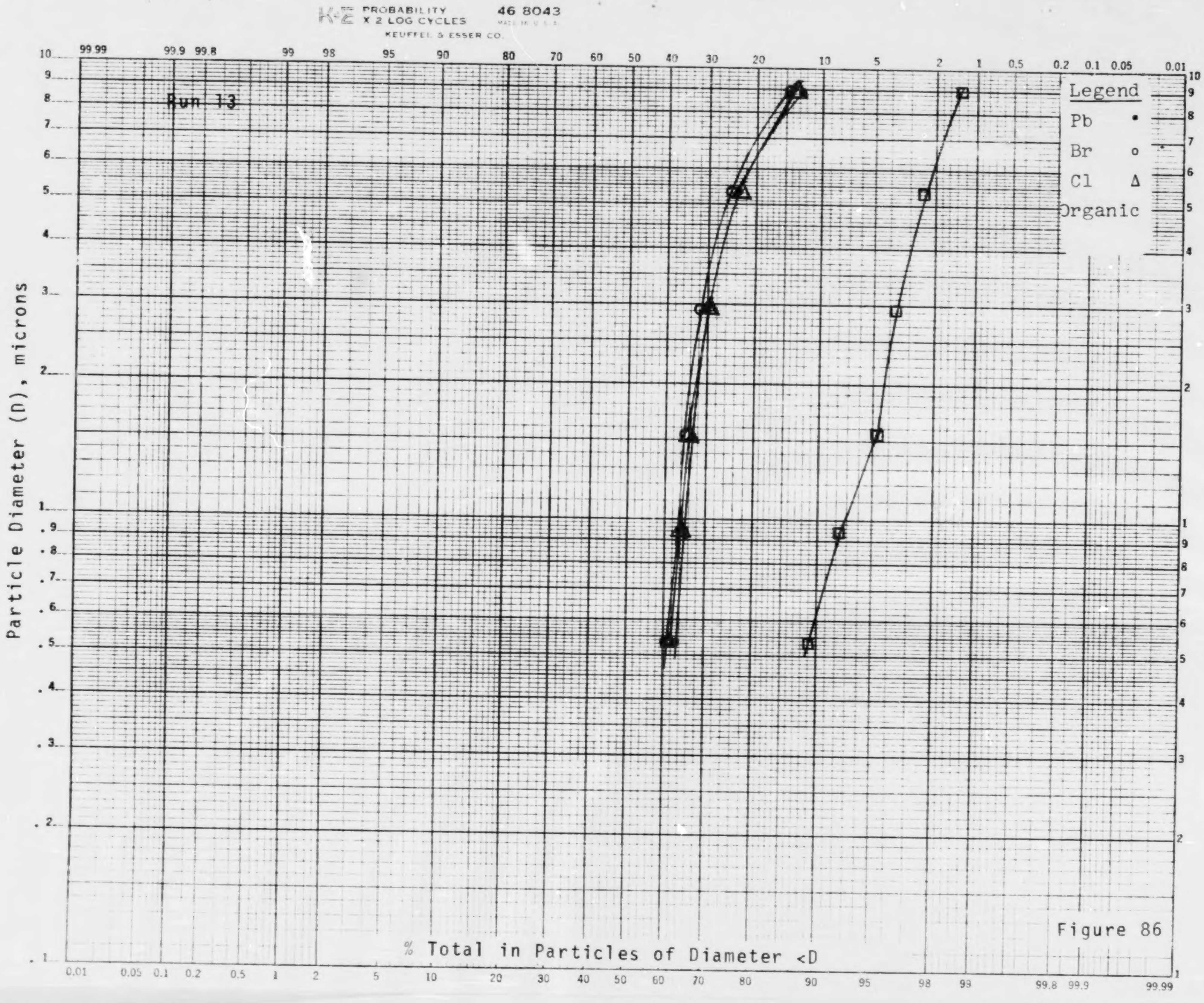

K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
Run 13
Legend
Pb •
Br o
Cl Δ
Organic
Particle Diameter (D), microns
% Total in Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
.1
.2
.3
.4
.5
.6
.7
.8
.9
1
2
3
4
5
6
7
8
9
10

Figure 86

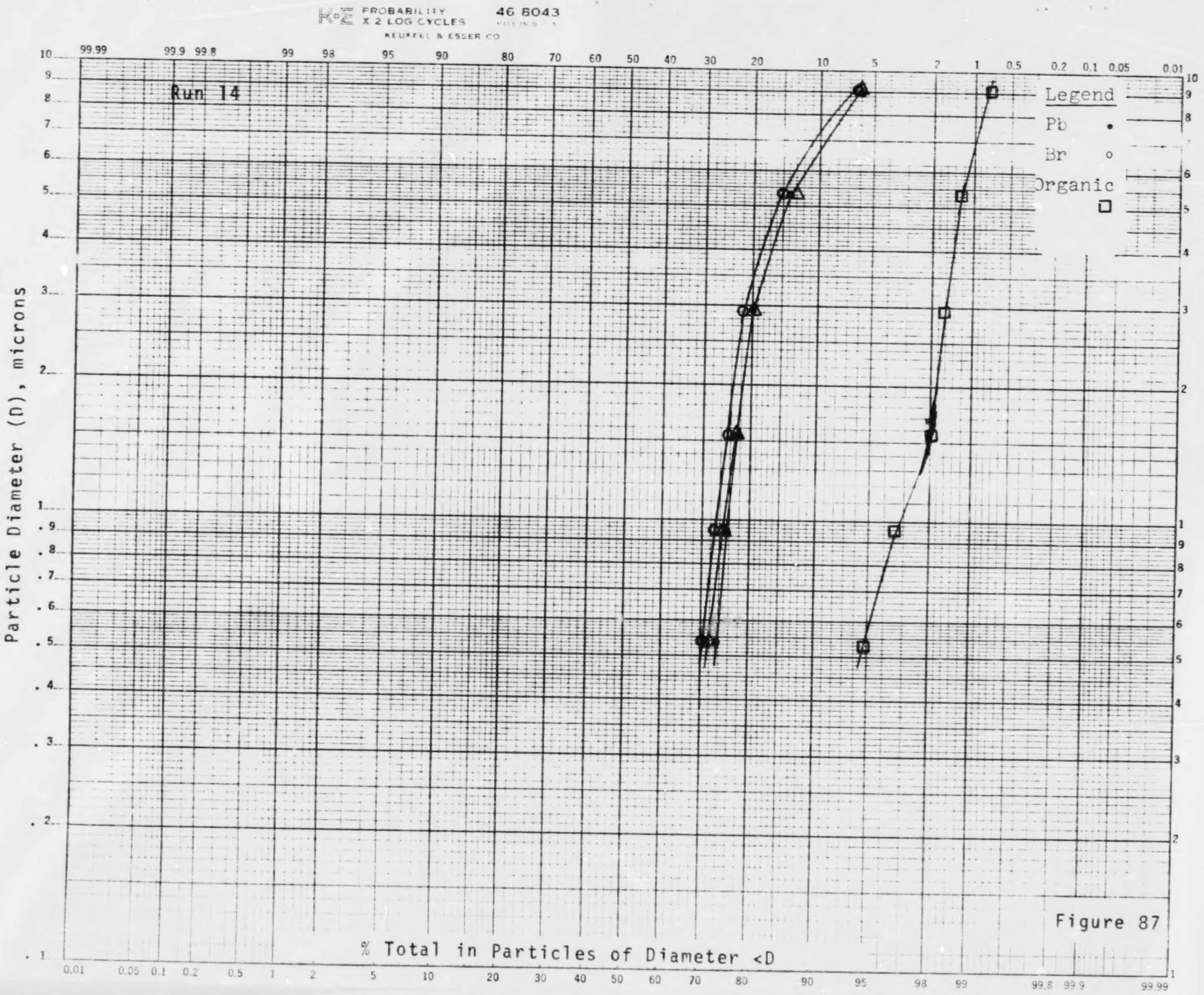

K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO
Run 14
Legend
Pb •
Br o
Organic □
Particle Diameter (D), microns
% Total in Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1

Figure 87

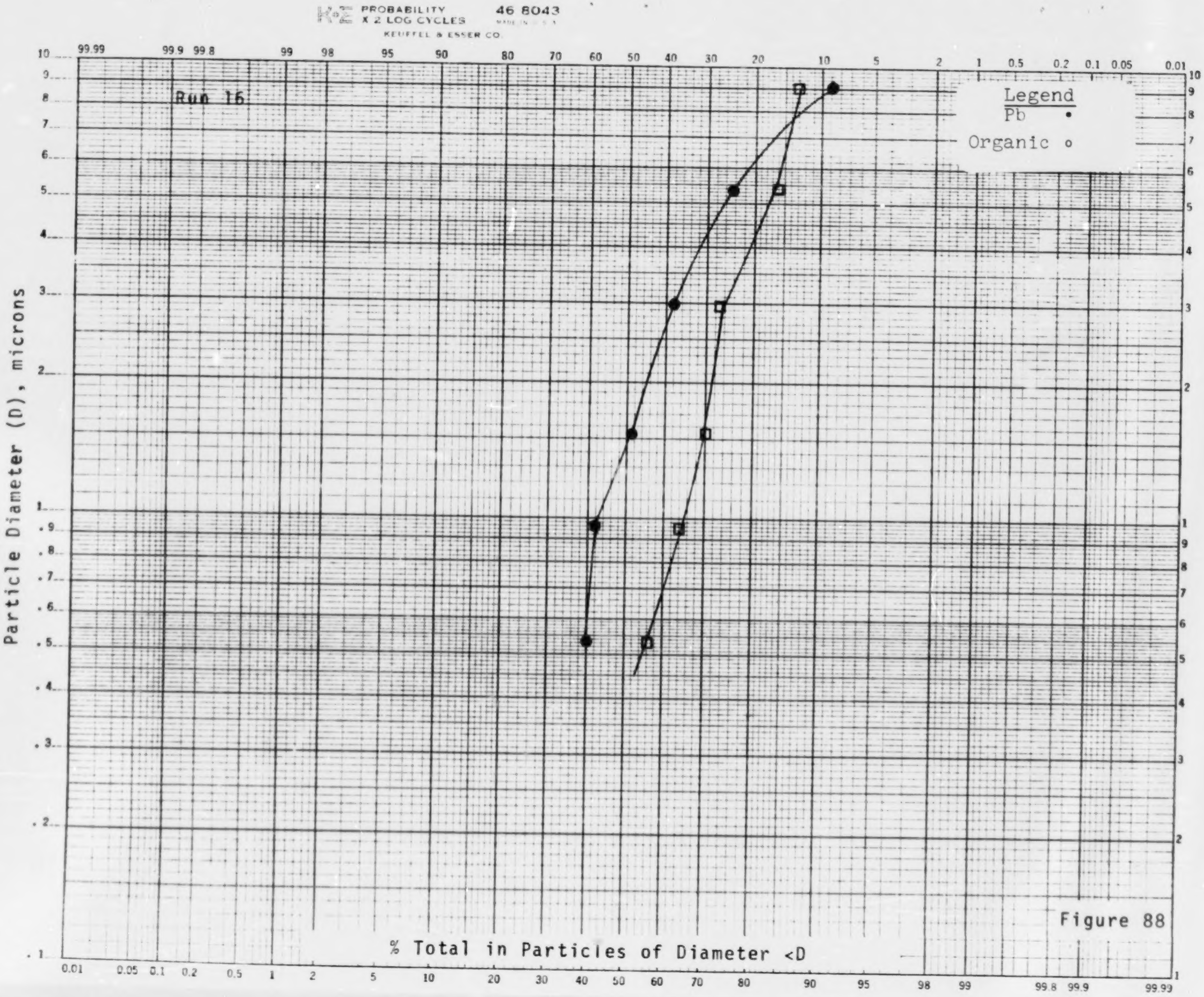
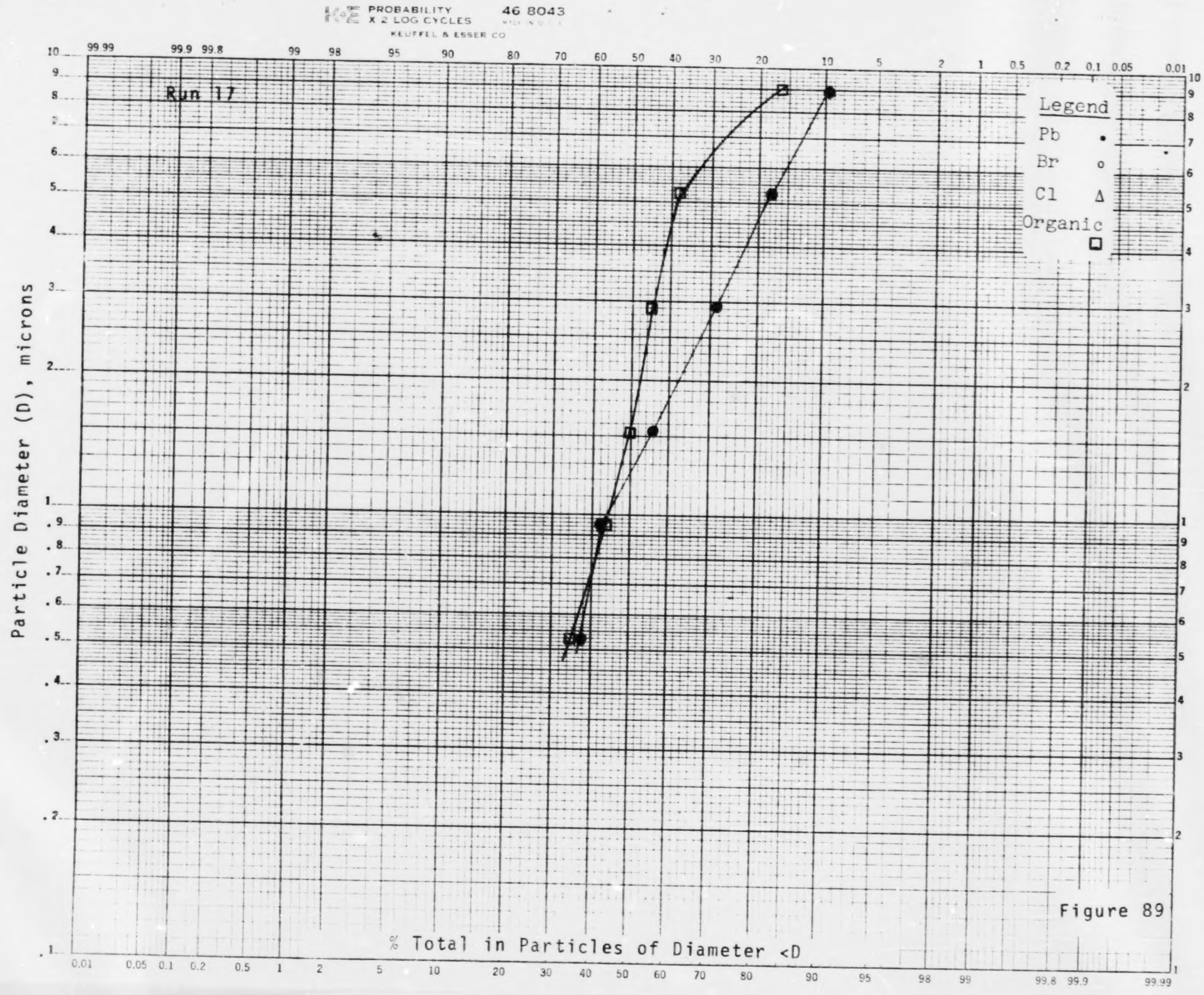

K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
Run 16
Legend
Pb •
Organic o
Particle Diameter (D), microns
% Total in Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

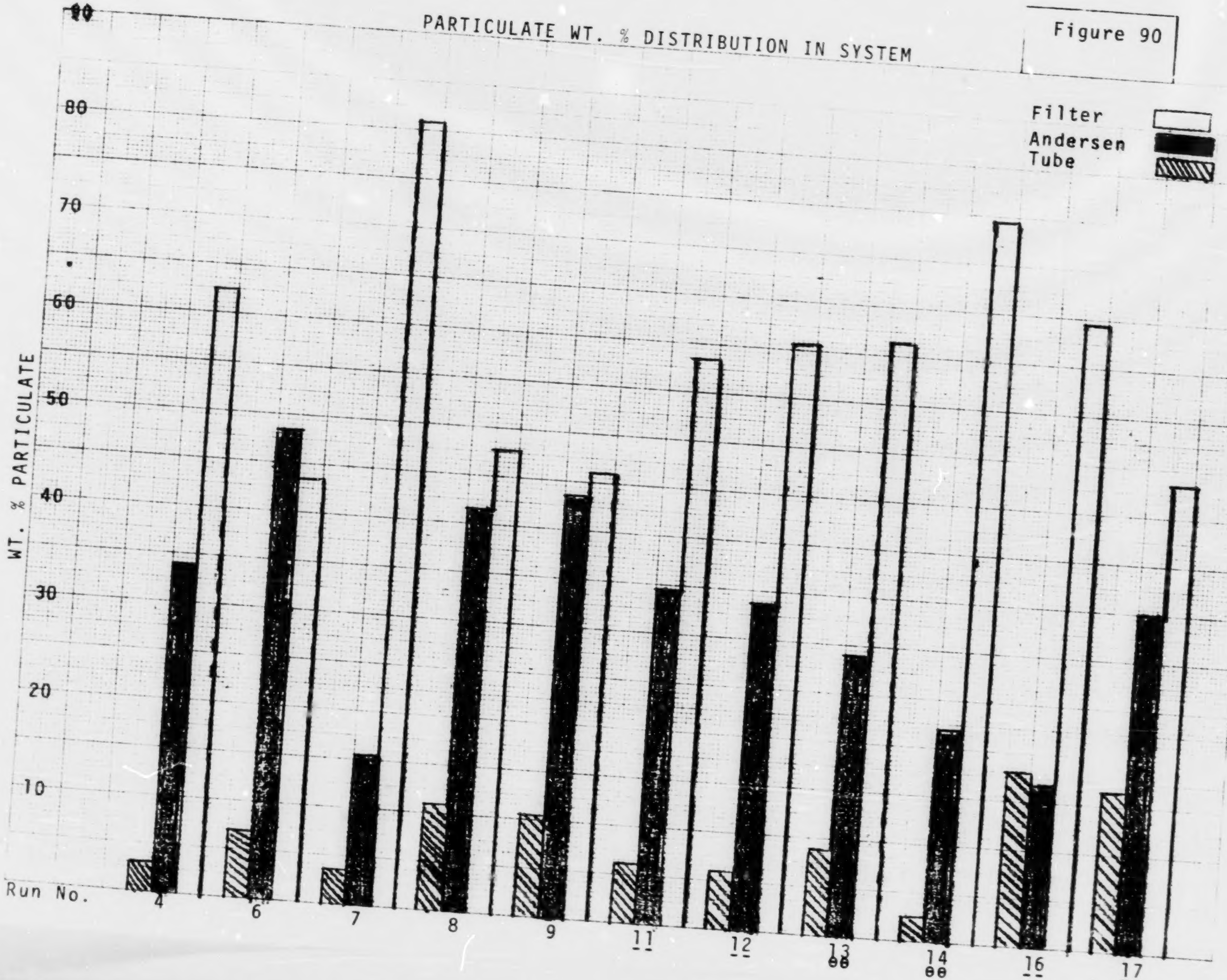
Figure 88



K+E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO
Run 17
Legend
Pb •
Br o
Cl Δ
Organic □
Particle Diameter (D), microns
% Total in Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

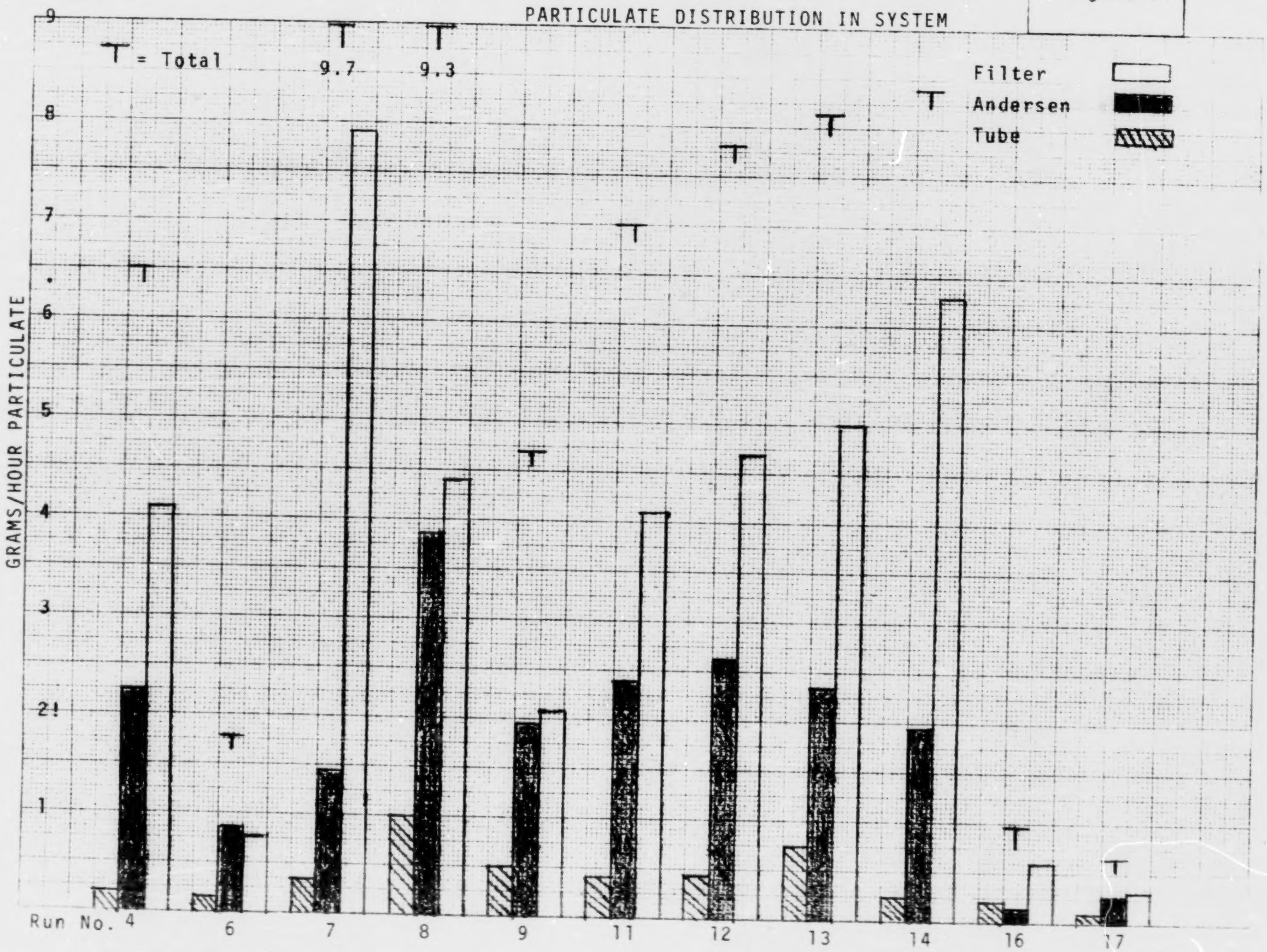
Figure 89

Figure 90


PARTICULATE WT. % DISTRIBUTION IN SYSTEM

K&E 10 X 10 TO THE CENTIMETER 46 1512

Figure 91

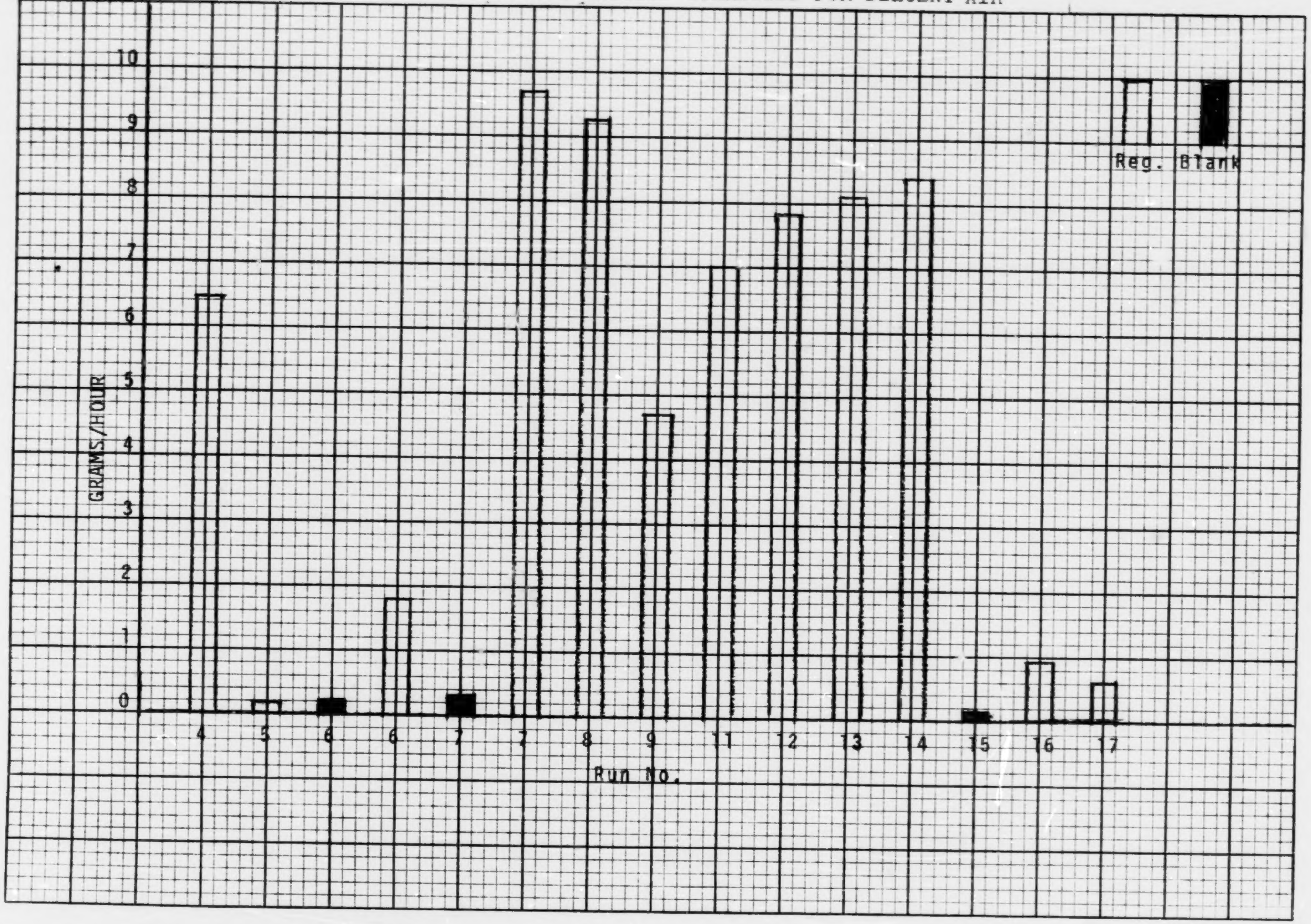


PARTICULATE DISTRIBUTION IN SYSTEM

K•E 5 x 5 TO ½ INCH 7 X 10 INCHES 46 0863 MADE IN U.S.A.
KEUFFEL & ESSER CO.

Figure 92

TOTAL PARTICULATE EMITTED CORRECTED FOR DILUENT AIR



samples are not available, so tube samples have been ignored in these distributions. In most cases, the tube sample accounts for less than 5% of the sample mass, so the error is slight. Distribution of the organic present in the emitted particles is only approximate. This distribution is based upon the organic level/mg sample determined by mass spectrum, the details of which are discussed in an earlier section.

Values for the mass median equivalent diameter (MMED) and the Pb, Cl, Br, organic mass median equivalent diameter are obtained in many cases by extrapolation of the above distribution curves. These values are listed in Table 23.

In all cases, on an equivalent diameter basis, 50% of the mass of emitted particles is associated with particles smaller than 1 micron (except run 6, Indolene HO 15).

Table 23
MASS MEDIUM DIAMETER

Run #	MMED	Pb MMED	Cl MMED	Br MMED	Organic MMED
4	0.10	∿0.10	<<0.10	<0.10	0.68
6	1.5	3.1	0.5	2.7	0.2
7	<<0.10	<<0.10	-	-	<<0.10
8	0.65	0.35	-	∿0.10	0.3
9	1.1	2.0	1.2	-	<0.10
11	∿0.10	∿0.10	∿0.10	∿0.10	<0.10
12	∿0.10	∿0.10	∿0.10	∿0.10	<0.10
13	∿0.10	∿0.10	∿0.10	∿0,10	<<0.10
14	<0.10	<0.10	<0.10	<0.10	<<0.10
15	<<0.10	-	-	-	-
16	<0.10	1.5	-	-	0.4
17	0.7	1.2	-	-	1.5

< less than 0.10μ
<< much less than 0.10μ
∿ approximately

The total particulate emissions in grams/hour are shown in Figure 92 for all test fuels. These values represent the summation of all particles collected in the dilution tube, Andersen's, and filters with appropriate factors applied for proportional sampling factors, for example. (Emissions in grams/mile can be obtained by dividing these values by 60 for all runs except 12, 14, and 17 in which case one divides by 40.5).

VI. DISCUSSION OF RESULTS

The results reported herein are based upon the generation, collection, and analyses of exhaust particles in a well-defined system and under carefully controlled engine laboratory conditions. Our basic aim in this first year's effort was to develop repeatable and reproducible means of generating and analyzing exhaust particles. This required that one establish an operational procedure which eliminated as many variables as possible and still was not an uncommon mode of operation for the internal combustion engine. Basic decisions with that in mind, dictated that the engine attached to a laboratory dynamometer be operated under reasonable conditions of load, speed, and stability. The "conditioning sequence" employed allowed the engine sufficient time under several mild load conditions with no severe acceleration modes to form stable deposits, exhaust hydrocarbons, etc. The particle sampling operation under air diluted conditions at 50 mph road load provided a not uncommon operational mode for the engine and yet allowed particle sampling under conditions somewhat related to the actual vehicle emission environment on the roadway. This careful control of the engine-fuel-emissions environment and the development of sound analytical approaches has resulted in our ability to ascertain significant differences with minor changes in fuel additives.

Faced with the realization that many factors could affect particulate emissions, we chose not only to reduce as many engine and sampling variables as possible but, in addition, at this stage to eliminate the basic fuel composition variable. This dictated that a single base fuel be used for initial studies. Indolene HO was chosen as that fuel. The first step in assessing our ability to observe particulate variations was the introduction of various Tetra Ethyl Lead levels in the base fuel as TEL is well known to emanate from the engine particles. The first phase of the effort then was to examine particulate emissions with TEL as the variable.

The next step was to determine the effect of TEL scavengers on particle emissions. This variable resulted in runs with Indolene HO plus 3.0 ml/gal TEL with no scavenger, motor mix scavenger, and EDB and EDC each in 1 theory concentrations. Satisfied that we could indeed discern differences with these variations we proceeded to the addition of a very small amount of a common detergent additive to the Indolene HO 30 leaded fuel. Although the additive was present at a level of only 12 pounds/1000 barrels of fuel, we believe on the basis of obviously limited data (Run 11 vs. Run 13), a significant effect on particle emissions, engine deposits, and hydrocarbon emissions was observed.

This quest, then, for a system capable of determining differences in particle emissions, deposits, and hydrocarbon emissions, has led us to the threshold of applying these techniques to the actual vehicle under simulated road conditions. This is the basis for our continued effort in this program.

Now that the basis upon which the data reported herein has been established, it is appropriate to address several specific topics.

The particle sampling system, the dilution tube, is perhaps the key to the data generated. In reality it dictates the definition of particulates collected and evaluated herein. Because it is designed in several pieces, it allows the capture and relatively simple collection of all particles emitted from the tailpipe. Because the samples collected in the Andersen's and filter are proportional samples, it was essential that this zone of the dilution tube be a stable and homogeneous mixture of diluent air and exhaust particles. The tube length (27 feet), flow rate (7 fps), and mixing baffle were designed to accomplish this objective. Additionally, this design results in a constant volume device noted by the small change in flow rate (volume) when sampling under the conditioning mode of engine operation.

Analysis of particles collected in the tube slit samples (removed from direct contact with the air-exhaust stream) suggested that organic levels were substantially higher for particles within the tube than for those removed. It is possible that adsorption of organics is occurring in the particle collected in the tube during the 48 hour sampling period. The significance of the organic level associated with the exhaust particles must, at this point, entertain this possibility. The dramatic increase in organic associated with particles as the particle size decreases however, (as noted by mass spectrometry, UV absorbance, and UV fluorescence) suggests that additional factors are involved. That the organics are associated with non-organic particles (lead salts) is substantiated by the Transmission Electron and Scanning Electron studies.

The determination of organics associated with particles has been and continues to be a challenging task. The mass spectrometry evaluations have provided a reasonable semi-quantitative evaluation of the total level of organics present. The trends observed (increased organic with decreasing particle size) seem to be clearly supported by the UV absorbance and fluorescence studies. The use of this data to provide cumulative organic distribution plots is not, however, completely sound. Thus, these distribution plots should be reviewed with this in mind.

The cumulative distribution plots of percent Pb, Cl, and Br neglect the particles collected in the tube. The percentage of the total particles collected in the tube, however, varies from 3 to 16 percent and, in most cases, has little effect on the MMED value. The cumulative distribution plots and D_{50} cut-off values were chosen on the basis of work reported by Flesch, et al (1967) and Wagman, et al (1967).

Trace metal analysis of the exhaust particles collected during runs 11 and 12 may provide an interesting cursory insight into the distribution of elements other than Pb, Cl, Br, and organics. Iron (from engine wear and the exhaust system) is clearly associated with larger particles as the percentage drops almost two orders of magnitude from tube samples to the filter following the Andersen. Calcium (oil) concentration increases with decreasing particle size. Zinc (oil, exhaust system) follows the iron trend. Silicon (air) is noted to be fairly constant in all particles. These analyses provide insight into the contribution of engine wear debris, fuel composition, oil additives, and air-borne debris on the complex composition of exhaust particles.

The frequent monitoring of the hydrocarbon emissions during the conditioning sequence was essential in maintaining stable engine operation. During the run with Indolene HO + 3.0 ml/TEL gallon, for example, it became necessary to change spark plugs every 6 to 8 hours. The fouling problem was noted before it was apparent to the engine operator by observing an unusual and sudden increase in hydrocarbon emissions. Following hydrocarbon emissions during conditioning and sampling indicated that combustion chamber deposits were not completely stable for the Indolene HO 30 fuel runs as the hydrocarbons continually increased. This is confirmed upon examination of the combustion chamber deposits for this fuel in runs 3, 4, and 11/12 which show an increased deposit weight with increased engine operating time.

The generation, collection, and analysis techniques developed and reported herein provide the basis for evaluation of fuel additives, fuel compositions, etc., on the particle emissions from vehicles under simulated road conditions which is the necessary next step in this continuing study.

VII. SUMMARY

A summary of test results is shown in Table 24. This summary sheet shows particulate emissions in grams/hour and grams/mile for samples collected in dilution tube slits and tube sections (sweepings), the Andersen Samplers, and filter following the Andersen. The total particles emitted for each test fuel is also shown as grams/hour and grams/mile, and is a summation of the individual sections. The Andersen and filter data figures are based upon the total exhaust stream although they are proportional sampling devices. The percentage increase from 0 hours (clean engine) to 75 hours (conditioned engine) for unburned hydrocarbons and NO are also summarized. Combustion chamber deposits are presented in grams (8 cylinders) and the total test hours for each run are shown.

Increasing the level of TEL in the fuel results in increased particle emissions, increased combustion chamber deposits, and increased hydrocarbon emissions during the conditioning sequence. No clear trend is obvious as to the effect of TEL on NO emissions. Intermediate levels of TEL (1.5 ml/gal) shows an unusual increase in hydrocarbon emissions build-up and in combustion chamber deposits, but a small increase in particulate emissions compared, of course, to the trace TEL run (Indolene HO 0). TEL scavengers have a definite effect on emissions and deposits. Runs #8 and #9 are graphic examples and should be compared to runs #3, #4, #11, and #12. Run #8 is the Indolene HO base fuel with 3 ml/gal TEL plus 1 theory of EDB in place of the motor mix scavenger package used in the Indolene HO 30 fuel (1 theory EDC plus 1/2 theory EDB). Run #9 is with 1 theory EDC only instead of motor mix scavenger. The results indicate that EDB does a more efficient job of removing TEL reaction products from the combustion chamber which results in lower chamber deposits and a lower hydrocarbon emission increase during engine conditioning.

Table 24
TABULATION OF PARTICULATE EMISSIONS DATA

Run No. and Fuel Used	Dilution Tube				Andersen Separator		Filter Paper		TOTALS**		% Increase 75-Hour Avg. All Cycles		Engine Deposits	
	Slits		Sweeping											
	gr/hr	gr/mile	gr/hr	gr/mile	gr/hr	gr/mile	gr/hr	gr/mile	gr/hr	gr/mile	HC	NO	Grams	Hours Total
3 Indolene HO 30	---	---	---	---	1.65208	.02751	---	---	---	---	76.25	23.65	115	103.7
4 Indolene HO 30	.01482	.000247	.1809	.00301	2.2405	.03734	4.1062*	.06843*	6.5424	.10904	78.0	11.76	143	128.8
5 Indolene HO 0	.01237	.000206	.03340	.000556	-.02708	-.00045	.16053	.00267	.17922	.00298	15.01	-7.05	20	126.1
6 Blank	0	0	0	0	.03958	.000659	.17916	.00298	.21874	.00365	---	---	---	---
6 Indolene HO 15	.01155	.000192	.1230	.00205	.89163	.01486	.79786	.013297	1.82399	.03039	59.42	7.14	96	127.0
7 Blank	0	0	0	0	.06875	.001145	.28333	.00472	.35208	.00586	---	---	---	---
7 Indolene HO 0 +3.ml/gallon TEL	.0084	.00014	.3525	.00587	1.47813	.02463	7.90826	.13180	9.7473	.16246	94.07	4.37	87	126.1
8 Indolene HO 0 1.0 Theory EDB +3.ml/gallon TEL	.0112	.000186	1.0344	.01724	3.8938	.06489	4.3997	.07332	9.3385	.15564	65.03	16.07	135	129.2
9 Indolene HO 0 1.0 Theory EDC +3.ml/gallon TEL	.01868	.000311	.4987	.00831	2.0395	.03399	2.14786	.03579	4.7046	.07841	131.5	-4.0	173	127.3
11 Indolene HO 30 Steady State Sampling	.01538	.000256	.4241	.00706	2.3998	.03999	4.1955	.06992	7.03477	.11725	33.98	-4.4	---	---
12 Indolene HO 30 Cycling for Sampling	.02119	.000353	.4488	.00748	2.6165	.04360	4.7394	.07899	7.8258	.13043	---	---	186	179.5
13 Indolene HO 30 DMA4A Steady State Sampling	.03117	.000519	.7269	.01211	2.3806	.03967	5.0213	.08368	8.15997	.13599	72.16	4.28	---	---
14 Indolene HO 30 DMA4A Cycling for Sampling	.01529	.000254	.2266	.00377	1.8725	.03120	6.3233	.10538	8.43776	.14063	---	---	120	139.7
15 Blank	0	0	0	0	.00433	.000072	.1420	.002366	.14633	.00244	---	---	---	---
16 Indolene HO 0 Steady State Sampling	.01314	.000219	.16459	.00274	.16754	.002792	.63091	.010515	.97617	.01627	9.22	0	---	---
17 Indolene HO 0 Cycling for Sampling	.00771	.000128	.0939	.00156	.22067	.003677	.3029	.00504	.62518	.01042	---	---	20	180.2

*Used filter paper weights from Run #11 (Indolene HO 30 repeat). **Corrected for diluent air particulate background.

As a result, the particulate emissions are substantially increased. EDC, on the other hand, does a much less efficient job which results in increased chamber deposits and hydrocarbon emissions build-up, and decreased particulate emissions. Not only are the emission levels affected, but the particulate emissions mass distribution is quite different.

The use of TEL with no scavengers results in higher hydrocarbon emissions and particulate emissions but lower combustion chamber deposits. The particle distribution is much different as most of the particles are below 0.1μ in size. The use of TEL alone also resulted in severe spark plug fouling problems which necessitated plug changes every 8-10 hours of engine operation.

The addition of a detergent type additive (DMA-4A) to the Indolene HO 30 fuel resulted in decreased combustion chamber deposits and hydrocarbon emissions build-up but, as noted for the scavengers above, an increase in particulate emissions.

It is apparent that additives which effectively remove reaction products from the combustion chamber also reduce hydrocarbon emissions of the stable, conditioned engine but, as a result, increase particulate emission levels.

Particulate emissions are modestly affected by the mild cyclic operation of the engine used in these studies. Runs #11 and #12, #13 and #14, and #16 and #17 are runs in which the first of the pair was sampled under steady-state (60 MPH, road load) conditions and the second under mild cycling conditions (Table 3) which averages about 40.5 mph. The cycling sequence is identical to the cycling sequence used in the first 75 hours of each run to condition the engine. Cyclic operation does, however, change the particle mass distribution and resulted in an increase in particulate emissions of somewhat less than 10% except for Indolene HO 0 (trace TEL) in which case a decrease was noted.

The data indicates that the fraction of organic material associated with particles increases substantially as particle size decreases. The amount of organic material present in the collected particles increases with the reduction of TEL levels in the fuel. The total organic present in all particles collected in each run appears to be roughly the same, however. In effect, the presence or absence of TEL and scavengers does not substantially change the total amount of organic material present in all collected particles, but the percentage organic is much higher for low TEL fuel runs because the mass of particles emitted is much lower. We believe this is due to the fact that the base fuel for all runs is essentially the same.

VIII. FUTURE

The relationship of this study to the practical world of the automobile is only casual at this point. It is essential that the following studies be conducted to serve as background information in support of proposed standards and measurement procedures for particulates.

1. Determine the effect of basic fuel composition on the chemical and physical characteristics of particulate emissions.

2. Determine the impact of the new low octane, low and non-lead fuels and low compression ratio engines on particulate emissions.

3. Relate these studies to the actual vehicle by conducting similar studies with the same classification system developed here with vehicles loaded by a chassis dynamometer under simulated road conditions.

It is felt that a sound technical basis has been developed in these studies from which we can knowledgeably extend this work to include these major points.

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Flesch, J., Norris, C., and Nugent A., (1967), American Industrial Hygiene Association Journal, Vol. 28, Nov.-Dec. 1967.

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37 Exhaust Particles. SEM Run #8
20,000X. Andersen Plate #3

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